Polish J. Chem., **78**, 987–995 (2004)

Kinetics and Mechanism of Complex Formation between O-Bonded Pentaammine(valinato/prolinato)cobalt(III) Ions and Nickel(II) in Aqueous Medium

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(Received January 19th, 2004; revised manuscript May 7th, 2004)

The kinetics of reversible complexation of $Ni(OH_2)_6^{2+}$ with oxygen-bonded valinato/prolinatocobalt(III) substrates, $(NH_3)_5Co(val/pro)^{3+}$ have been investigated by stopped flow technique at 25°C, $6.1 \leq pH \leq 6.70$ and $I = 0.3$ mol dm^{-3}. The formation of binuclear species, $[(NH_3)_5Co(val/pro)Ni]^{4+}$, occured *via* the reaction of $Ni(OH_2)_6^{2+}$ with deprotonated (amine and imine functions of valine and proline, respectively) form of the cobalt(III) substrates, $(NH_3)_5Co(val/pro)^{2+}$. The results indicate the formation of mono-bonded binuclear species through entry of the imine/amine functions into the coordination sphere of Ni(II) with Ni–OH_2 bond dissociation is limiting (I_d mechanism). The binuclear species exist in dynamic equilibrium involving the mono-dentate and chelated forms with chelated forms predominating. The small values of dissociation rate constants, despite the intrinsic electrostatic repulsion between the like charge centers, also support the chelate nature of the binuclear species.

Key words: kinetics, heteronuclear Ni(II)–Co(III) complexes, valinato- and prolinato–cobalt(III) complexes

In recent years a lot of attention has been devoted to the studies of heterobimetallic (same/mixed metal) complexes, because of their importance in developing methodology for synthesis of molecular based magnets [1] and catalytic precursors [2]; gaining insight into the pathways of electron transfer reactions of chemical and biological importance [3] *etc*. One of the synthetic strategies for such complexes is to use a **ligand**, that contain potential donor groups (bridging ligand), which are capable to coordinate with other added metal ion or complexes. The bridging ligands used are of the type hydroxo, fluoro, cyano, carboxylato, carbonato, phenolate, aminocarboxylate *etc*. The synthesis and magnetic properties of mixed valent heterobimetallic complexes have been reported in [4].

The reaction between Ni(II) and partially bonded bi-/polydentate ligands to a relatively inert metal center like Co(III) leads to formation of heterobinuclear complexes; the bi-/polydentate ligands bridging both the metal centers in the resulting binuclear species [5–7]. The kinetics of reversible formation of such binuclear complexes with a number of partially bound carboxylates and aminoacidates, as the brid-

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ging ligands has been studied recently [7–12]. These studies provide opportunity to examine the Ni(II) complexation with respect to the nature and number of unbound donor sites of the ligands, overall charge and steric properties of cobalt(III) moiety, ring size and stability of the resultant heterobinuclear complexes *etc*. As a part of our current research interest and sequel to our previous investigations [7–12], the present study aims to see the effect of basicities of unbound N-atoms of two biologically important ligands on overall kinetics and mechanism of their complexation with Ni(II).

EXPERIMENTAL

Pentamminevalinatocobalt(III) perchlorate and pentaammineprolinatocobalt(III) iodide were prepared by following the reported methods [13]. Sample purities were checked by analysis of Co and UV-visible spectral data, which are in good agreement with the theoretical values and those reported earlier [13]. Stock solution of $Ni(ClO_4)_2$ was prepared by digesting AR grade nickel carbonate with slight excess of $HClO_4$, and Ni(II) content was estimated complexometrically. Sodium perchlorate (AR) was used to maintain the ionic strength of reactant solutions. All solutions were prepared in doubly distilled water. The pH measurements were made with an Elico digital pH meter (model – LI 120) using combined glass electrode and standard NBS buffers of pH ≈ 4.01, 6.87 and 9.18. The activity of $H^+(a_H^+)$ was converted into concentration, using activity coefficient calculated by the Davies equation [14]. All UV-visible spectra were recorded on a Perkin Elmer (Lambda 20) spectrophotometer using 10 mm matched quarter cells.

Kinetics. The kinetics of reversible complexation between Ni(II) and the cobalt(III) substrates were studied under pseudo first order conditions by stopped flow technique at 25°C, $\lambda = 280$ nm and $I = 0.3$ mol dm^{-3} using a fully automated Hi-Tech (UK) SF-51 stopped flow spectrophotometer. The MES buffer (4-morpholinoethane sulphonic acid) was used to control the pH of the reaction mixture. Further details were the same as described in our earlier work [11]. The absorbance (decreases with time for valinato complex at 280 nm and increase with time for prolinato complex at 400 nm) *versus* time data for the formation of binuclear complex fitted well to a single exponential function, characteristics of the first order kinetics, even after spreading the reaction rate on a time scale accessible by the instrument (0.01–500 s). The rate constants reported are the average of at least five replicate runs and the errors quoted are standard deviations.

RESULTS AND DISCUSSION

Acid dissociation constants (K_{NH}) of cobalt(III) complexes: The acid dissociation constant (K_{NH}) for unbound amine/imine groups of the title complexes were determined by potentiometric titration at 25°C, $I = 0.3$ mol dm^{-3}. The pK_{NH} values [see (1)] were found to be 8.12 ± 0.04 and 8.75 ± 0.03 for valinato and prolinato complexes, respectively.

$$[N_5Co(O_2CR^1NH_2^+/O_2CR^2NH_3^+)]^{3+} \overset{K_{NH}}{\rightleftarrows} [N_5Co(O_2CR^1NH/O_2CR^2NH_2]^{2+} + H^+ \quad (1)$$

(where, $N_5 = (NH_3)_5$, $R^1 = C_4H_7$ and $R^2 = (CH_3)_2$ CH–CH <)

Reversible formation of binuclear complexes: The interactions of nickel(II) with cobalt(III) substrates are clearly evident from the Uv-visible spectra shown in Fig. 1 (a,b). The pseudo first order rate constants (k_{obs}) for the reversible formation of binuclear species between nickel(II) and $N_5Co(O_2CR^1NH_2/O^2CR^2NH_3)^{3+}$ and cobalt(III) substrates at varying pH and [Ni^{2+}] are collected in Tables 1 and 2. The k_{obs} values at a given pH increased linearly with [Ni^{2+}] (see Fig. 2a and 2b). The slopes and intercept of the plots, being identified with the overall rate constants of formation (k_f) and dissociation (k_r) of the binuclear species, respectively. The inverse acid dependence of k_f values may be attributed to the involvement of NH/NH_2 deprotonated form of prolinato/valinato in the cobalt(III) substrates, $N_5Co(O_2CR^1NH/O_2CR_2NH_2)^{2+}$.

The intercepts of the k_{obs} *versus* [Ni^{2+}] plots at different pH, however, converge to a common point, indicating that the dissociation rate constant of the binuclear species is pH independent in the range 6.1 ≤ pH ≤ 6.7. Previous studies [7,10–12] on Ni(II)

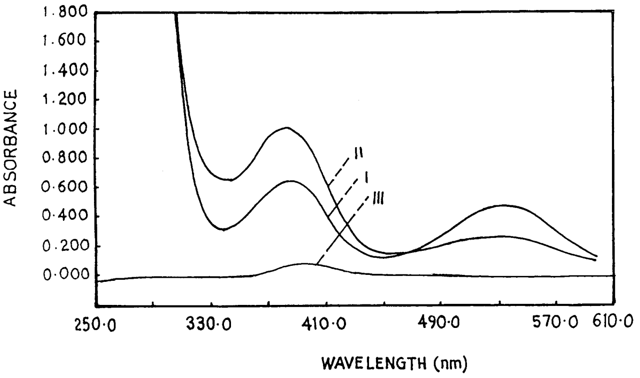


Figure 1a. Spectral evidence for formation of the binuclear species between Ni(II) and $[Co(NH_3)_5ProH]_T^{2+}$ ions at pH ≈ 6.1, I = 0.3 mol dm^{-3} ($NaClO_4$). (I) $[Co(NH_3)_5ProH^{2+}]_T$ = 4×10^{-3}; (II) $[Co(NH_3)_5(ProH)^{2+}]_T = 4\times10^{-3}$ + $[Ni^{2+}]_T = 2\times10^{-2}$; (III) $[Ni^{2+}]_T = 2\times10^{-2}$ mol dm^{-3}.

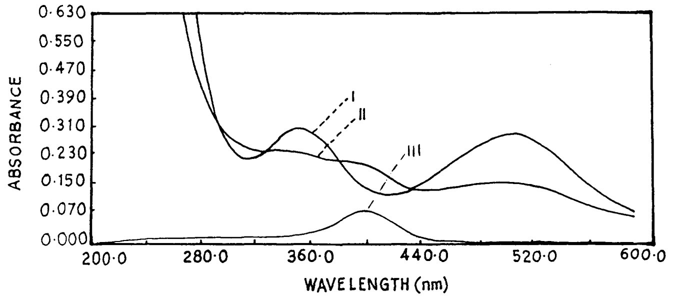


Figure 1b. Spectral evidence for the formation of binuclear species between Ni(II) and $[Co(NH_3)_5(ValH)]_T^{2+}$ ions at pH ≈ 6.10, I = 0.3 mol dm^{-3} ($NaClO_4$). (I) $[Co(NH_3)_5(ValH)^{2+}]_T$ = 4×10^{-3}; (II) $[Ni^{2+}]_T = 2\times10^{-2}$ + $[Co(NH_3)_5(ValH)^{2+}] = 4\times 10^{-3}$; (III) $[Ni^{2+}] = 2\times10^{-2}$ mol dm^{-3}.

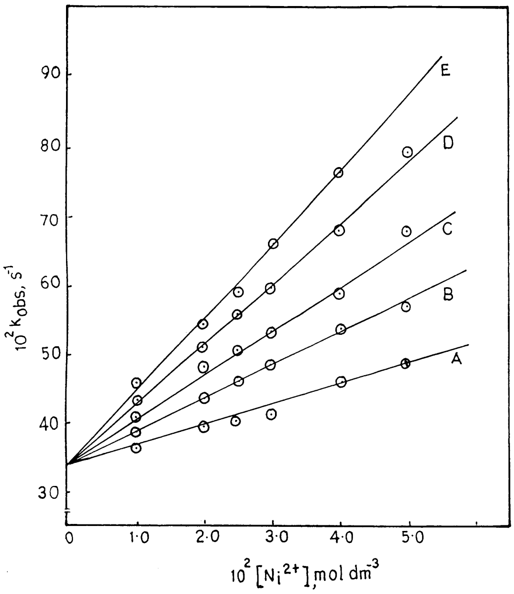


Figure 2a. k_{obs} *versus* 10^2 $[Ni^{2+}]_T$ plots at 25°C and at pHs: 6.13±0.02 (A), 6.34±0.01 (B), 6.49±0.03 (C), 6.59±0.02 (D) and 6.70±0.02 (E) for $[Co(NH_3)_5(ProH)^{2+}]$.

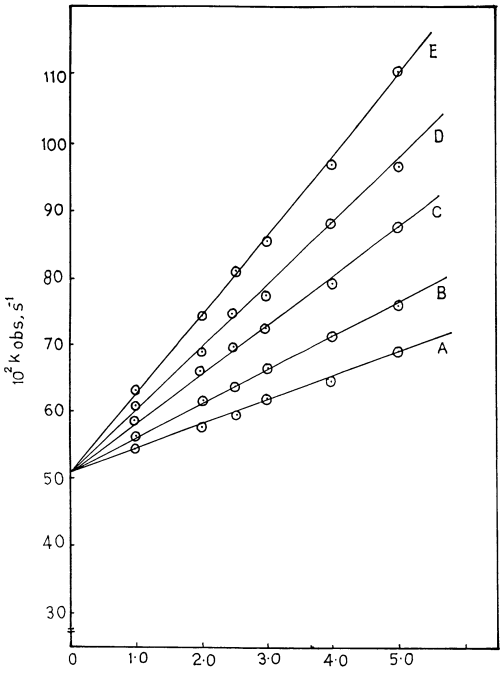
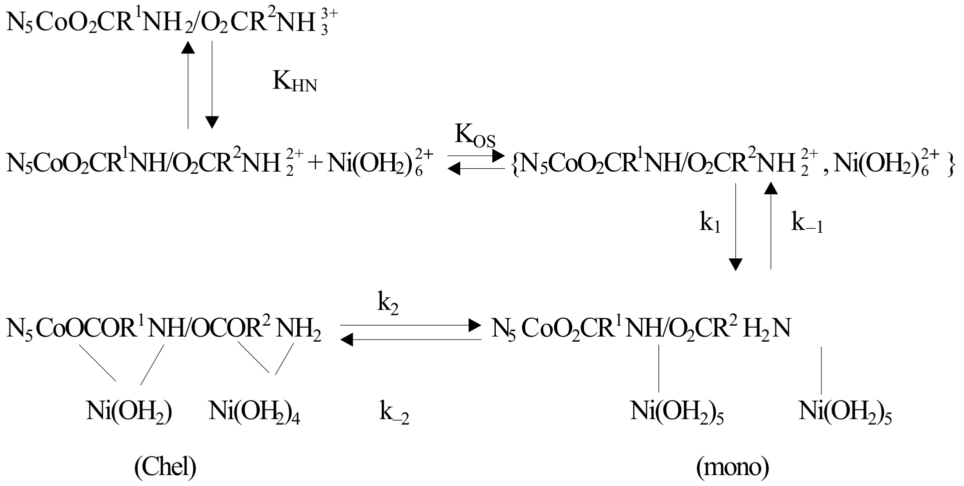


Figure 2b. k_{obs} *versus* 10^2 $[Ni^{2+}]_T$ plots at 25°C and at pHs: 6.15 ±0.03 (A), 6.32 ± 0.02 (B), 6.48±0.01 (C), 6.59±0.02 (D) and 6.71±0.02 (E) for $[Co(NH_3)_5(ValH)^{2+}]$.

complexation with a variety of partially bound aminocarboxylate revealed, that the pendant amine function and the carboxylato group bound to cobalt(III) center most likely chelate Ni(II). Similar chelates formation in the binuclear species is also expected in the present case (see Structure (I) and (II)). Considering the above facts, a possible reaction mechanism may be delineated as in Scheme 1.

Scheme 1



For which, k_{obs} takes the form (2)

$$k_{obs} = k_f(K_{NH}/[H^+] + K_{NH})[Ni^{2+}] + k_r \tag{2}$$

Where, the overall formation rate constant (k_f) and the dissociation rate constant (k_r) for the binuclear species are given by (3) and (4), respectively

$$k_f = K_{OS}k_1k_2/(k_2 + k_{-1}) \tag{3}$$

$$k_r = k_1k_{-2}/(k_{-1} + k_2) \tag{4}$$

In (3) and (4), k_1 and k_{-1} denote the first order rate constant for the formation and dissociation of mono-bonded species, derived from the encounter complex, $\{N_5CoO_2CR^1NH/O_2CR^2NH_2, Ni(OH_2)_6\}^{4+}$, respectively; k_2 and k_{-2} are the intramolecular chelation and dechelation rate constants for the mono ⇔ chel equilibrium, respectively, and K_{OS} is the equilibrium constant for the outer sphere association constant of $[N_5CoO_2CR^1NH/O_2CR^2NH_2]^{2+}$, and $Ni(OH_2)_6^{2+}$. Initially the values of k_f and k_r were calculated from the gradients and intercepts of least square best line plots of k_{obs} *versus* [Ni^{2+}]. Since k_r turned out to be independent of pH, k_f values were then calculated from all rate data using the mean values of k_r and the values of K_{NH}, obtained from potentiometric measurement. The values of k_f, k_r along with K_{NH} reproduce the rate constants (see Tables 1 and 2) satisfactorily supporting the validity of the proposed rate law (see eq. 1).

Table 1. Rate data for the reversible formation of binuclear complex between $Ni(OH_2)_6^{2+}$ and pentaammineprolinatocobalt(III) at 25°C, I = 0.3 mol dm^{-3}, λ = 400 nm.

pH_{av}	6.13±0.02	6.34±0.01	6.49±0.03	6.59±0.02	6.70±0.02
10^2 [Ni^{2+}] mol dm^{-3}					
	$10^2 k_{obs}^{(a)}$ s^{-1}				
1.0	36.8±1.5	38.9± 1.6	40.5±1.8	43.7±1.3	45.2±1.0
2.0	39.4±0.8	43.1± 0.9	48.1±1.6	51.0±1.4	54.1±2.5
2.5	40.5±1.2	45.8± 2.1	50.5±0.9	56.1±2.3	60.1±1.7
3.0	41.8±1.9	48.4± 1.9	53.5±1.3	60.0±1.9	66.2±3.2
4.0	46.0±1.3	54.1± 2.5	59.2±2.7	68.3±3.1	76.3±1.9
5.0	48.1±1.1	57.3± 1.8	68.1±2.3	79.3±2.8	88.1±2.8

k_f(av), dm^3 mol^{-1} s^{-1} = 1658±48, k_r(av) = 0.0336±0.032.

Table 2. Rate data for the reversible formation of binuclear complex between $Ni(OH_2)_6^{2+}$ and pentaamminevalinatocobalt(III) at 25°C, I = 0.3 mol dm^{-3}, λ = 280 nm.

pH_{av}	6.13±0.03	6.32±0.02	6.48±0.01	6.59±0.02	6.71±0.02
10^2 [Ni^{2+}] mol/dm^3					
	$10^2 k_{obs}^{(a)}$ s^{-1}				
1.0	54.5±2.1	56.1± 2.8	58.5±1.9	60.2±2.2	63.0±2.1
2.0	57.5±1.8	61.5± 3.1	65.5±3.2	68.5±1.9	74.5±1.6
2.5	59.1±2.6	63.5± 2.3	69.5±2.2	74.7±1.9	81.5±3.9
3.0	61.8±0.9	66.1± 1.9	72.0±1.9	77.5±2.3	85.5±2.8
4.0	64.1±2.1	71.2± 2.1	79.0±2.2	88.2±1.9	97.2±4.1
5.0	68.5±1.6	75.5± 2.3	87.5±3.1	96.2±2.7	111± 3.8

k_f(av), dm^3 mol^{-1} s^{-1} = 428±14, k_r(av), s^{-1} = 0.509±0.022.

It is worth noting, that the k_r values of $[N_5CoO_2CR^1NH/O_2CR^2NH_2, Ni(OH_2)_4]^{4+}$ are *ca.* 14–21, 25–36 and (9.8–14.9)×10^3 times smaller than those for monomethylaminenickel(II) [15], monoethylaminenickel(II) [15] and monoacetatonickel(II) [16] respectively, while they are only 5–9 times larger than the values of dissociation rate constant of monoglycinatonickel(II) [17] species, despite the fact that the interionic repulsion between the two positively charged centers {Co(III) and Ni(II)} of the binuclear complexes under consideration act in favour of their dissociation (see Table 3). The location of rate determining step in the dissociation of binuclear species can now be considered referring to (5); a rearranged form of (4),

$$k_r = k_{-1} \cdot Q/f \tag{5}$$

where $f = 1 + k_{-1}/k_2$ and $Q = k_{-2}/k_2$, *i.e.* the equilibrium constant for mono dentate and chelate forms of binuclear species. Assuming that the value of k_1 is comparable to the water exchange rate constant of the $Ni(OH_2)_6^{2+}$ {k_{ex} = 2.7–3.6) $\times 10^4$ s^{-1} at 25°C} [18], and that of k_{-1} equal to that of $CH_3CH_2NH_2$ $Ni(OH_2)_5^{2+}$ ($k_{-1} \cong 10$ s^{-1} at 25°C) the ratio of k_{-1}/k_2 turns out to be *ca.* 3.3×10^{-4}. Hence, f = 1.0 would seem to be a reasonable estimate, for which $k_r = k_{-1}Q$. Thus, it appears that the dissociation rate of the mono-bonded form (k_{-1}) limits the overall dissociation of the binuclear species to the reactants. The small value of the dissociation rate constant must be due to a relatively lower value of Q. Assuming $k_{-1} \cong 10$ s^{-1}, $f \cong 1.0$ and $k_r \cong 0.4$ s^{-1}, a tentative value of Q is found to be 0.04, which means that the mono ⇔ chel equilibrium is strongly driven to the chelated form. Further slightly lower dissociation rate constant (k_r) value of the binuclear complex, formed between Ni(II) and prolinato complex, indicates its greater stability compared to that formed with valinato complex, which is also evident from the stability constant values (K_M) for Ni(II) complexes with the free ligands [19].

Table 3. Comparative rate parameters for the reversible formation of binuclear species between Ni(II) and $N_5CoO_2CR^1NH/O_2CR^2NH_2^{2+}$ with some related systems.

Reacting species[a]	I, mol dm^{-3}	k_f, dm^3 mol^{-1} s^{-1}	k_r, s^{-1}	Ref.
Glycinate ion	0.1	$(1.5–4.1)\times 10^4$	5.7×10^{-2}	16,17
Prolinate ion	–	3.4×10^4	–	17
Acetate	0.0	–	5.0×10^3	16
Methylamine	0.1	13.1×10^2	7.7	15
Ethylamine	0.1	8.65×10^2	9.6–13.3	15
$(NH_3)_5Co(gly)^{2+}$	0.3	$(2.71\pm 0.41)\times 10^2$	0.10 ± 0.007	20
$(Tetren)Co(gly)^{2+}$	0.3	$(2.70\pm 0.37)\times 10^2$	0.14 ± 0.015	20
$(Tetren)Co(pyc)^{2+}$	0.3	$(6.70\pm 0.34)\times 10^2$	0.079 ± 0.001	21
$(NH_3)_5Co(pro)^{2+}$	0.3	$(16.58\pm 0.48)\times 10^2$	0.336 ± 0.032	This work
$(NH_3)_5Co(val)^{2+}$	0.3	$(4.28\pm 0.14)\times 10^2$	0.509 ± 0.022	This work

[a] gly = glycinate, pyc = pyridine-2-carboxylate, pro = prolinate, and val = valinato.

The overall rate constant for the forward reaction, as defined in (2), takes the form given by (6):

$$k_f = K_{OS}k_1/f \tag{6}$$

The values of k_f for both the cobalt(III) substrate are higher than those reported for corresponding glycinato complexes [20] under identical conditions. However, these values are smaller than those for glycinate ($NH_2CH_2COO^-$) [17] and prolinate ions [16] and comparable with those reported for methylamine and ethylamine [15] (see Table 3). This rate difference may be attributed partly to a lower K_{OS} value for the substrates under consideration. Based on the diffusion limiting ion pairing, a purely coulombic concept, K_{OS} can be calculated using the Fuoss equation [21]. At 25°C and $I = 0.3$ mol dm^{-3}, the K_{OS} value for (2+/2+) ion pair turned out to be 0.047 dm^3 mol^{-1} [11]. Using $K_{OS} = 0.05$ dm^3 mol^{-1} and $I = 1.0$ for the present investigation, the k_1 values ($= k_f/k_{OS}$) turned out to be 8.56×10^3 and 3.31×10^4 s^{-1}, respectively for valinato and prolinato complexes. These first order rate constants (k_1's) are comparable to the water exchange rate constant of $Ni(OH_2)_6^{2+}$ [$10^4 k_{ex} = 2.7–3.6$ s^{-1} at 25°C] [18]. It is, thus, interesting to note that alteration in the mode of coordination of valinato and prolinato with $Ni(OH_2)_6^{2+}$ (*i.e.* O – for unbound valine/proline and N – for the title complexes) has virtually no effect on the intimate mechanism. An I_d mechanism involving Ni(II)–OH_2 bond dissociation largely controls the rate determining process for the formation of binuclear complexes.

Acknowledgments

The authors thank Dr. N.N. Das, Scientist, National Metallurgical Laboratory, Jamshedpur for his keen interest and help during the course of work.

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