Polish J. Chem., **77**, 1221–1228 (2003) **INORGANIC CHEMISTRY**

Kinetics and Mechanism of Complex Formation between Pentamminesuccinatocobalt(III) and Gallium(III)

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(Received April 7th, 2003; revised manuscript June 11th, 2003)

The reversible complexation between pentamminesuccinatocobalt(III) with gallium(III) was investigated by stopped flow technique in the temperature range $15 \leq t \leq 35°C$, and over an acid range of $0.15 \leq [H^+] \leq 0.30$ mol dm^{-3}. Consistent inverse rate dependence was observed with increasing $[H^+]$. The major path, as supported by the formation rate constant, is $[(NH_3)_5CoOCO(CH_2)_2CO_2H]^{2+} + Ga(OH)^{2+} \rightarrow (NH_3)_5CoOCO(CH_2)_2CO_2Ga^{4+} + H_2O$. Results obtained here firmly corroborate the chelating nature of half bonded succinato moiety with the gallium ion. By comparing the $\Delta G^{\#}$ values of k_1 and k_2 paths with the $\Delta G^{\#}$ of the k_{ex} path and k_1 and k_2 with the k_{ex} (25°C), it was proposed that the substitution at Ga^{3+} centre is interchange dissociative (I_d).

Key words: kinetics and mechanism, stopped flow, complexation, gallium(III), pentamminesuccinatocobalt(III)

The insertion of metal ions into the coordination sphere of a complex is of immense importance in view of metal ligand interaction in solution. Extensive studies on the complexation of alkaline earth and first row divalent transition metal ions have been reported [1–4]. Rapidly reacting trivalent metal ion systems have been on the contrary comparatively scarcely studied and investigations have been confined inter alia to reactions of iron(III) [5–8] and rare earth ions [3]. As far as complexes of non-transition trivalent metal ions are concerned, only rate measurements of Al(III), Ga(III), and In(III) with sulphate ion [9–10(a), 10(b)], of In(III) with mureoxide [11], and of Al(III) with ferricyanide and cobalticyanide [12,13] are reported in literature. The complexation reactions of *cis*-(amine)-(3-NO_2-salicylato)bis(ethylenediamine) cobalt(III) ion with Al(III) [14(a)], oxalatopentamminecobalt(III) ion with Al(III) and Ga(III) [15], and 4-nitro-catechol with Ga(III) [16] have been studied recently. Data accumulated from these extensive studies have suggested the amenability of complexation reactions to charge, size and coordination environment of metal ions, from both kinetic and thermodynamic standpoints. The mechanistic picture ranges from A to D covering I_a and I_d, depending on the nature of complexing metal ion. Mechanistic studies of the complexation reactions at acidatopentamminecobalt(III) centre by

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non-transition metal ion such as gallium(III) have not been widely investigated [15,16]. The present piece of work is a typical one with the inclusion of succinato as the bridging ligand between $(NH_3)_5Co^{3+}$ and Ga^{3+} center, which on the other hand enables us to examine the complexing ability of the reacting substrates and the stability of the binuclear species formed. Analogous data on complexation reaction of other cobalt(III) substrates with Fe^{3+} [5], Al^{3+} [14(a)] and Ni^{2+} [14(b)] are available for comparison.

EXPERIMENTAL

Materials: $[(NH_3)_5CoO_2C(CH_2)_2COOH](ClO_4)_2$ was prepared by the published method [17]. The analytical data agree well with the previous reported values [18]. The purity of the complex was further checked by estimation of Co^{3+} by Laitinen and Burdett method [19]. Gallium perchlorate was prepared and the metal ion content and free acid were estimated adopting standard procedure [20,21]. Ionic strength was adjusted using $NaClO_4$. All solutions were prepared by doubly distilled water, the second distillation being made from an all glass distillation apparatus.

Kinetic measurements: The kinetics of reversible complexation of the succinatopentamminecobalt(III) complex with gallium(III) was investigated at four different temperatures (15, 20, 30 and 35°C), $\lambda = 300$ nm and $I = 1.0$ mol dm^{-3}. The rate (absorbance decay with time) measurements were made on a fully automated SF-51 stopped flow spectrophotometer, compatible with an IBM 486PC. Only a single exponential curve was displayed (with a decrease in absorbance with time) for every run, even after spreading the monitoring time over the time scale {log (1,2), log (2,1)} available with the IS_2 software package from HITECH (U.K.). Each reported rate constant value is a statistical average of 5 to 6 replicate runs. pH measurements were made using a Nucleonix digital pH meter. The UV-visible spectrum was recorded on a Perkin Elmer Lambda 20 spectrophotometer with 10 mm matched quartz cells.

RESULTS AND DISCUSSION

The spectra of the succinato complex in the absence and presence of Ga(III) is shown in Fig. 1, which illustrates its interaction with the metal ions, corroborating the earlier findings [20]. Table 1 lists the pseudo first order rate constants as a function of $[Ga^{3+}]$ and $[H^+]$ at different temperatures. Under the experimental $[H^+]$ the concentration of the conjugate base from pentamminesuccinatocobalt(III) would be extremely small (pK_a *ca.* 4.2 at 25°C, $I = 1.0$ mol dm^{-3}) [21] and the concentration of $Ga(OH_2)_5(OH)^{2+}$ is also small ($pK_h = 2.938$ at 25°C and $I = 0.5$ mol dm^{-3}, hydrolysis constants at other requisite temperatures are also known) [15]. Furthermore, the proton ambiguity for the reaction between above reactants is quite unlikely to be due to sizable difference in the pK_a's of the reactants. On these grounds, a reasonable scheme is presented below (Scheme 1), for which the pseudo-first order rate constant is given by (1).

Aqua ligands in the coordination sphere of gallium(III) are not shown for convenience.

$$k_{obs} = (k_1 + k_2K_h/[H^+])(K_1/\{K_1 + [H^+]\})[Ga^{III}]_T + k_{-1} + k_{-2}K'_h/[H^+] \qquad (1)$$

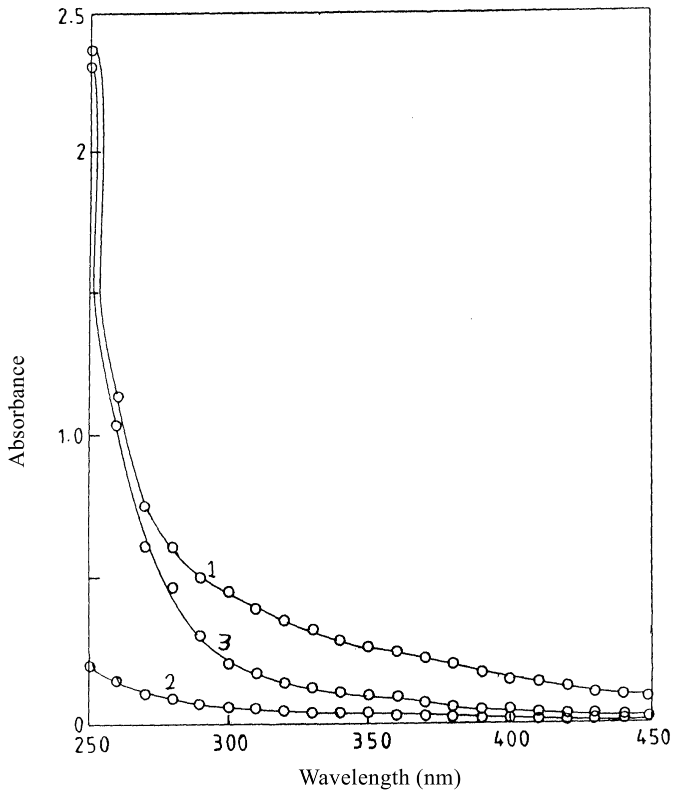


Figure 1. UV-VIS spectra of $[(NH_3)_5CoOCO(CH_2)_2CO_2H]^{2+}$ in the presence and absence of Ga(III); (1) [Complex] = 4.0×10^{-3}, (2) $[Ga^{III}] = 3.0\times10^{-2}$ mol dm^{-3} and (3) mixture of the above two at $[H^+] = 0.10$, $I = 1.0$ mol dm^{-3} and temperature 25°C.

where the k_i's are the respective rate constants and K_1, K_h and K_h' are the equilibrium constants for the different equilibrium processes, as shown in Scheme 1. The validity of the equation was checked by making a crude approximation, where the contribution of k_1, K_h' and k_{-2} were neglected. Strikingly, the k_{obs} *versus* $\{K_l/K_l+[H^+]\}[Ga^{III}]/[H^+]$ plot was reasonably linear (r = 0.982) (see Fig. 2).

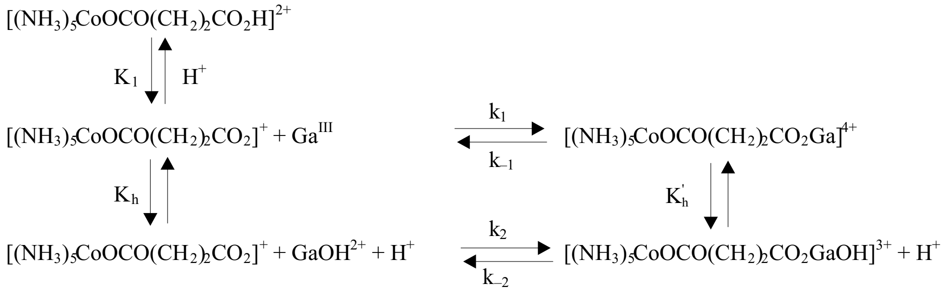
Table 1. Values of k_{obs} (s^{-1}) at different $[Ga^{3+}]_T$, $[H^+]$, and temperatures. [Complex] = 4×10^{-4}, I = 1.0 mol dm^{-3} ($NaClO_4$).

10^3 $[Ga^{3+}]$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	k_{obs} (s^{-1})			
		15°	20°	25°	35°
2.5	0.30	1.35±0.08	1.84±0.17	2.47±0.18	4.53±0.31
3.0	0.30	1.50±0.11	2.05±0.13	2.76±0.21	5.04±0.19
4.0	0.30	1.73±0.16	2.37±0.10	3.18±0.28	5.82±0.36
5.0	0.30	1.98±0.13	2.71±0.12	3.63±0.31	6.64±0.27
6.0	0.30	2.21±0.18	3.03±0.12	4.07±0.34	7.42±0.53

Table 1 (continuation)

7.0	0.30	2.48±0.21	3.40±0.19	4.55±0.29	8.32±0.61
8.0	0.30	2.71±0.23	3.71±0.13	4.97±0.38	9.04±0.73
9.0	0.30	2.99±0.31	4.11±0.26	5.52±0.29	10.06±0.91
2.5	0.25	1.46±0.07	1.98±0.07	2.67±0.16	4.87±0.37
3.0	0.25	1.65±0.13	2.23±0.12	3.01±0.21	5.49±0.46
4.0	0.25	1.99±0.08	2.70±0.15	3.64±0.32	6.64±0.39
5.0	0.25	2.39±0.17	3.23±0.21	4.36±0.19	8.00±0.51
6.0	0.25	2.76±0.23	3.73±0.19	5.02±0.28	9.18±0.66
7.0	0.25	3.14±0.29	4.24±0.24	5.72±0.42	10.49±0.71
8.0	0.25	3.49±0.15	4.72±0.16	6.38±0.56	11.73±0.80
9.0	0.25	3.88±0.33	5.24±0.32	7.08±0.47	12.85±1.01
2.5	0.20	1.69±0.13	2.33±0.12	3.19±0.09	5.85±0.39
3.0	0.20	1.91±0.09	2.61±0.23	3.57±0.14	6.53±0.51
4.0	0.20	2.41±0.16	3.31±0.19	4.47±0.21	8.16±0.62
5.0	0.20	2.88±0.21	3.94±0.28	5.40±0.40	9.84±0.31
6.0	0.20	3.40±0.27	4.64±0.13	6.36±0.71	11.63±0.97
7.0	0.20	3.89±0.46	5.32±0.37	7.28±0.43	13.30±0.85
8.0	0.20	4.41±0.35	6.02±0.43	8.23±0.37	–
9.0	0.20	4.89±0.51	6.72±0.50	9.21±0.39	–
2.5	0.15	2.28±0.17	3.08±0.16	4.19±0.17	7.64±0.43
3.0	0.15	2.65±0.14	3.59±0.24	4.87±0.25	8.93±0.61
4.0	0.15	3.35±0.30	4.53±0.19	6.17±0.38	11.30±0.86
5.0	0.15	4.13±0.46	5.57±0.32	7.57±0.42	13.87±0.92
6.0	0.15	4.93±0.28	6.67±0.28	9.06±0.39	16.57±1.09
7.0	0.15	5.69±0.37	7.69±0.17	10.44±0.56	19.04±0.77
8.0	0.15	6.49±0.41	8.82±0.23	11.99±0.47	–
9.0	0.15	7.16±0.63	9.74±0.41	13.25±0.53	–

Scheme 1



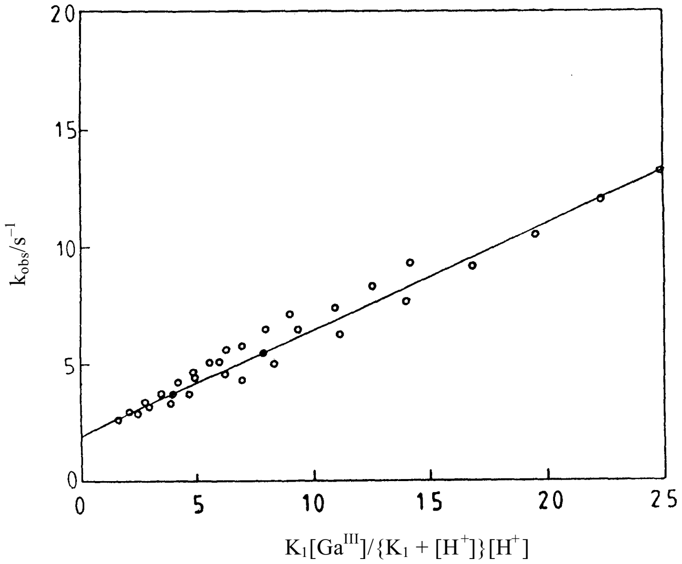


Figure 2. Plot of k_{obs} *versus* $K_1[Ga^{III}]/\{K_1 + [H^+]\}[H^+]$ at 25℃.

The complexation was studied at $[H^+]_T = 0.15–0.30$ mol dm^{-3} in order to avoid appreciable hydrolysis of $Ga(OH_2)_6^{3+}$ and polymerization of $GaOH^{2+}$, under this condition the cobalt(III) substrate will exist in bisuccinato form ($[H^+] >> K_1$).

In accord with Scheme 1, k_{obs} *versus* $[Ga^{3+}]_T$ plot at constant $[H^+]_T$ was also linear with positive intercept and positive slope at each $[H^+]$. The expression for the slope and the intercept at a particular $[H^+]$ has the following form:

$$\text{Slope} = \{k_1 + k_2K_h/[H^+]\}\{K_1/(K_1 + [H^+])\} \tag{2}$$

$$\text{Intercept} = k_{-1} + k_{-2}K'_h/[H^+] \tag{3}$$

However, under the experimental condition, the contribution of K_1 is virtually absent. As such (2) assumes the form:

$$\text{Slope} = \{k_1 + k_2K_h/[H^+]\}/[H^+] \tag{4}$$

In an attempt to evaluate the different constants adopting multiple regression technique, we obtained positive values of k_1, k_{-1}, k_2 and negative value of $k_2K'_h$, indicating thereby that k_{obs} had the essential form given by

$$k_{obs} = \{k_1 + k_2K_h/[H^+]\}[Ga]_T/[H^+] + k_{-1} \tag{5}$$

Hence, both the reaction paths *viz.* $(NH_3)_5OCOCo(CH_2)_2CO_2H^{2+}$ + $GaOH_2^{3+}$ and $(NH_3)_5OCOCo(CH_2)_2CO_2H^{2+}$ + $GaOH^{2+}$ are equally significant contrary to our earlier observations [15], where the interaction between coordinate oxalate and $Ga(OH_2)^{3+}$ was absent. Table 2 contains the pertinent data of kinetic parameters obtained by least square analysis. The activation parameters, $\Delta H^{\#}$ and $\Delta S^{\#}$, were evaluated by applying a weighted least-squares fitting to the Eyring equation.

Table 2. Values of kinetic parameters obtained for the complexation reaction between pentamminesuccinatocobalt(III) and gallium(III).

Temperature (°C)	k_1 ($mol^{-1}\ dm^3\ s^{-1}$)	k_2 ($mol^{-1}\ dm^3\ s^{-1}$)	k_{-1} (s^{-1})	k_2K_h (s^{-1})
15.0	0.44×10^2	7.93×10^3	0.99	10.70
20.0	0.60×10^2	12.11×10^3	1.40	14.66
25.0	0.78×10^2	17.84×10^3	1.87	20.52
35.0	1.46×10^2	32.93×10^3	3.31	36.22

The relatively low value of formation constant k_1 against k_2 (see also [23]) towards complexation must be attributed to the substantial Coulombic repulsion effect for the diffusion controlled encounter complex, formed between the substrate and metal ion as well as rate limiting $M^{n+}{-}OH_2$ dissociation for outersphere-innersphere conversion of the encounter complex.

The spread of formation rate constant (k_2) values for the complexation of Al^{3+}, Fe^{3+} with oxalatopentamminecobalt(III) is very low and almost comparable with our case. This indicates that the change in bridging ligand (succinato) for binuclear complex formation has a small role to play over variation in k_2, irrespective of the nature of metal ion. The higher values of k_2, in comparison to k_1, further supports the strong labilising action of the metal bound hydroxyl group.

The dissociation rate constant (k_{-1}) of the binuclear species falls in the order as depicted by Martell [24] (*viz.* $Ni^{II} > Ga^{III} > Fe^{III} > Al^{III}$). Evidently the inherent coulombic repulsion between the like charges in the binuclear species is outweighed by the strong metal-ligand interaction, which presumably pertains to the chelating action of the succinato moiety.

It is observed that the value of k_1 for the Co(III) substrates are ~100 times smaller than the water exchange rate constant of $Al(OH_2)_6^{3+}$ ($k_{ex} = 16\ s^{-1}$ at 25°C) [25]. A similar observation has been made in the study of kinetics of complexation of pentamminesalicylatocobalt(III) with Fe(III), for which $k_1 = 7\pm2\ mol^{-1}\ dm^3\ s^{-1}$ (30°C, I = 1.0 mol dm^{-3}) [8] and k_{ex} $\{Fe(OH_2)_6^{3+}\} = 160\ s^{-1}$(25°C) [26]. In the present work, we got $k_1 = 78.0\ mol^{-1}\ dm^3\ s^{-1}$(25°C), whereas $k_{ex}\{Ga(OH_2)_6^{3+}\} = 398.0\ s^{-1}$ at 25°C [27]. The fact that $k_1 < k_{ex}$ eliminates the simple S_N2 mechanism concept and supports an I mechanism. For the substitution reaction of $Fe(OH_2)_6^{3+}$ with various cobalt(III) substrates, the I_a mechanism has been proposed [28,8,29]. Such a possibility cannot be ruled out completely for $Ga(OH_2)_6^{3+}$ and substitution at the latter will have more of I_d character.

Much faster substitution reactions for $Ga(OH_2)_5(OH)^{2+}$, as observed in the present work, are consistent with the I_d mechanism as has been proposed for $Fe(OH_2)_5(OH)^{2+}$, [28,8,29,30] with cobalt(III) substrates.

Table 3. Comparison of kinetic parameters with other related systems at 25°C.

System	Metal ion	k_1 (mol^{-1} dm^3 s^{-1})	k_{-1} (s^{-1})	k_2 (mol^{-1} dm^3 s$^{-1)}$	k_2K_h (s^{-1})	Ref.
Salicylate	Al^{3+}	9.1×10^{-1}	7.8×10^{-1}	1.02×10^{3}	–	30
Cis-$[Co(en)_2(NH_3)O_2CC_6H_3(3\text{-}NO_2)OH]^{2+}$	Al^{3+}	(0.183±0.003)	2.68×10^{-3}	–	–	14(a)
*$[(NH_3)_5CoO_2CCO_2H]^{2+}$	Al^{3+}	(2.47±0.05)	$(5.0\pm1.0)\times10^{-2}$	–	–	15
*$[(NH_3)_5CoO_2CCO_2H]^{2+}$	Ga^{3+}	–	–	17.14×10^{3}	19.72 ±0.06	15
*$[(NH_3)_5CoO_2CCO_2H]^{2+}$	Fe^{3+}	11.0×10^{2}	0.7	4.8×10^{3}	–	28
*$[(NH_3)_5CoO_2CCO_2H]^{2+}$	Ni^{2+}	$(3.99\pm0.12)\times10^{3}$	(89.6± 1)	–	–	31
$[(NH_3)_5CoOCO(CH_2)_2CO_2H]^{2+}$	Ga^{3+}	0.780×10^{2}	1.87	17.84×10^{3}	20.52	This work

*at 30°C.

The activation free energy change $\Delta G^{\#}$ for both k_1 and k_2 paths are found to be 62.12 and 61.40 kJ mol^{-1} at 25°C, I = 1.0 mol dm^{-3}, and are in fair agreement with the reported values [27] of $\Delta G^{\#}$ for the $k_{ex}(s^{-1})$ path for substitution at Ga^{3+} centre. This fact further corroborates that both the paths are having exclusively I_d character.

Acknowledgments

One of the authors GSB is thankful to C.S.I.R. for granting a Senior Research Fellowship. The financial assistance of C.S.I.R. and Department of Science and Technology, Govt. of India is gratefully acknowledged.

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