

Kinetics and mechanism of formation of binuclear complexes of iron(III) with malonatopentaaminocobalt(III) and *trans*-bis(Hmalonato)bis(ethylenediamine)cobalt(III) ions in aqueous solution

Nigamananda Das & Rabindra K Nanda*

Department of Chemistry, Utkal University, Bhubaneswar 751 004

Received 20 July 1990; accepted 1 October 1990

The kinetics of formation of binuclear complexes between iron(III) and malonatopentaaminocobalt(III) and *trans*-bis(Hmalonato)bis(ethylenediamine)cobalt(III) have been studied using stopped-flow technique in the concentration ranges $[H^+] = 0.050-0.30$, $[Fe(III)] = 0.005-0.03$, and $I = 0.5 \text{ mol dm}^{-3}$ and over the temperature range 15.0 to 30.0°C. A general mechanism is proposed which accounts for the available data on the formation of binuclear species involving mainly the reactions of Fe^{3+} and $FeOH^{2+}$ with the undissociated form of the cobalt(III) substrates. The rate data for the various paths for *trans*-bis(Hmalonato)bis(ethylenediamine)cobalt(III) are slightly higher than those for the corresponding pentaamine analogues. The activation parameters for the various paths are also reported.

The kinetic studies on metal ion catalysed aquation at the cobalt(III) centre of binuclear precursor complexes formed between iron(III) and several carbonylatoaminocobalt(III) complexes¹⁻⁹ have revealed that a rapid and reversible equilibrium is established between the added aquo metal ion and the cobalt(III) complexes. However, kinetics of rapid formation of binuclear species of Fe(III) and Al(III) with unused donor function of bound dicarboxylate ligands in different cobalt(III) substrates have been very sparingly studied¹⁰⁻¹². Dash and Harris¹⁰⁻¹¹ have reported the kinetics of reversible complexation of iron(III) with oxalatopentaaminocobalt(III) and some salicylatopentaaminocobalt(III) substrates. Our objectives in undertaking the title study are to study the effect of the basicity of bound carboxylate ligand, size of chelate ring in the binuclear complex and the overall charge of the cobalt(III) substrate on the kinetics of its complexation with Fe(III).

Materials and Methods

Malonatopentaaminocobalt (III) and *trans*-bis(Hmalonato)bis(ethylenediamine)cobalt (III) perchlorates were prepared and characterised as described earlier^{3,8}. Stock solution of iron(III) perchlorate was prepared and the iron(III) and free acid contents of the stock solution were estimated as described previously⁸. All other chemicals used were reagent grade. All the solutions were prepared in doubly distilled water.

Kinetic measurements

The kinetics of formation of the binuclear species

was followed at 350 nm (absorbance increases with time) using a HITECH SF 51 stopped-flow spectrophotometer with Apple IIGS computer interface. The rate measurements were made under pseudo-first order conditions at 15-30°C [for $Co(en)_2(malH)_2^+$] and at 25°C [for $Co(NH_3)_5(malH)_2^{2+}$] (where $malH = O_2CCH_2COOH^{-1}$) employing $[Fe(III)]_T = 5.0 \times 10^{-3}$ to $30.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[H^+] = 0.05-0.30 \text{ mol dm}^{-3}$. Ionic strength was adjusted to 0.5 mol dm^{-3} with $NaClO_4$. Other kinetic details were similar to those described earlier¹⁰. The pseudo-first order rate constants were obtained by fitting the exponential trace displayed on the monitor to a first order equation using appropriate computer program supplied by M/S Hitech Scientific Ltd (UK). The observed rate constants reported are average of at least five kinetic runs and the errors quoted are standard deviations. All other calculations were made using appropriate least squares programs adopted to Apple IIGS PC.

Results and Discussion

Rate data for the formation of the binuclear species are collected in Tables 1 and 2. It is evident that the pseudo-first order constants increase linearly with $[Fe^{3+}]_T$ at a fixed acidity resulting in a constant finite intercept for k_{obs} versus $[Fe^{3+}]_T$ plots at $[H^+]_T = 0.05-0.30 \text{ mol dm}^{-3}$ (see Fig. 1). It is, therefore, reasonable to assume that the acid dependence of the reaction results only from the $Fe(OH_2)^{3+}/Fe(OH_2)_5OH^{2+}$ equilibrium. The slopes of such plots, however, very inversely with $[H^+]_T$. The observed first order dependence of k_{obs} with $[Fe^{3+}]_T$ is

Table 1—Rate data for complexation of $\text{trans-[Co(en)}_2(\text{malH})_2]^+$ with Fe(III) at $I = 0.5 \text{ mol dm}^{-3}$

$[\text{HClO}_4]_{\text{T}}$ (mol dm^{-3})	$10^3[\text{Fe}^{3+}]_{\text{T}}$ (mol dm^{-3})	k_{obs} (s^{-1})			
		$15.0 \pm 0.1^\circ\text{C}$	$20.0 \pm 0.1^\circ\text{C}$	$25.0 \pm 1^\circ\text{C}$	$30.0 \pm 0.1^\circ\text{C}$
0.05	4.793	2.89 ± 0.09	5.28 ± 0.28	9.87 ± 0.28	16.35 ± 0.25
	7.67	3.30 ± 0.11	6.50 ± 0.19	11.92 ± 0.30	20.09 ± 0.29
	10.54	3.67 ± 0.10	7.26 ± 0.18	13.30 ± 0.33	23.06 ± 0.41
0.075	4.793	2.88 ± 0.08	4.79 ± 0.27	8.33 ± 0.14	14.88 ± 0.26
	7.67	3.17 ± 0.06	5.38 ± 0.16	9.54 ± 0.19	17.01 ± 0.38
	10.54	3.50 ± 0.08	6.14 ± 0.14	10.62 ± 0.37	19.63 ± 0.28
	15.33	3.98 ± 0.10	7.05 ± 0.13	12.80 ± 0.22	23.31 ± 0.09
0.10	4.793	2.74 ± 0.05	4.54 ± 0.28	8.16 ± 0.24	13.43 ± 0.25
	7.67	2.98 ± 0.09	5.27 ± 0.19	9.37 ± 0.36	15.42 ± 0.16
	10.54	3.22 ± 0.08	5.71 ± 0.17	10.11 ± 0.44	17.41 ± 0.36
	14.85	3.55 ± 0.10	6.53 ± 0.14	11.65 ± 0.20	19.85 ± 0.53
	20.13	3.92 ± 0.11	7.16 ± 0.20	13.36 ± 0.20	23.55 ± 0.14
0.2	4.793	—	4.15 ± 0.23	7.26 ± 0.21	12.79 ± 0.69
	7.67	2.76 ± 0.11	4.53 ± 0.31	7.79 ± 0.23	14.36 ± 0.40
	10.54	2.87 ± 0.12	4.87 ± 0.19	8.60 ± 0.19	16.30 ± 0.62
	15.33	3.14 ± 0.06	5.36 ± 0.15	9.64 ± 0.24	17.80 ± 0.41
	20.13	3.30 ± 0.06	6.02 ± 0.20	10.61 ± 0.24	19.60 ± 0.57
	30.67	—	6.08 ± 0.12	11.19 ± 0.25	19.90 ± 1.09
0.3	10.54	—	4.49 ± 0.26	8.17 ± 0.47	14.23 ± 0.48
	15.33	—	5.06 ± 0.23	9.20 ± 0.25	15.67 ± 0.41
	20.13	—	5.20 ± 0.25	10.04 ± 0.29	16.89 ± 0.79
	30.67	—	6.08 ± 0.12	11.19 ± 0.25	19.90 ± 1.09

Table 2—Rate data for complexation of $(\text{NH}_3)_5\text{CoalH}^{2+}$ with Fe(III) at $I = 0.5 \text{ mol dm}^{-3}$, $25.0 \pm 0.1^\circ\text{C}$

$[\text{HClO}_4]_{\text{T}}$ (mol dm^{-3})	$10^3 [\text{Fe(III)}]_{\text{T}}$ (mol dm^{-3})	k_{obs} (s^{-1})	k_{f} ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	k_{r} (s^{-1})
0.05	4.793	8.02 ± 0.18	541.8 ± 15.8	5.43 ± 0.12
	7.67	9.67 ± 0.29		
	10.54	11.12 ± 0.25		
0.075	4.793	7.04 ± 0.21	377.0 ± 30.0	5.16 ± 0.31
	7.67	8.23 ± 0.27		
	10.54	8.99 ± 0.14		
	15.33	11.12 ± 0.23		
0.10	4.793	6.59 ± 0.30	315.3 ± 15.9	5.09 ± 0.20
	7.67	7.45 ± 0.23		
	14.85	9.97 ± 0.27		
	20.13	11.28 ± 0.31		
0.20	7.67	6.57 ± 0.33	207.3 ± 6.3	4.92 ± 0.10
	10.54	7.09 ± 0.32		
	15.33	8.06 ± 0.21		
	20.13	9.13 ± 0.23		
0.30	10.54	6.36 ± 0.17	136.6 ± 5.6	4.96 ± 0.11
	15.33	7.05 ± 0.27		
	20.13	7.77 ± 0.14		
	30.67	9.08 ± 0.23		

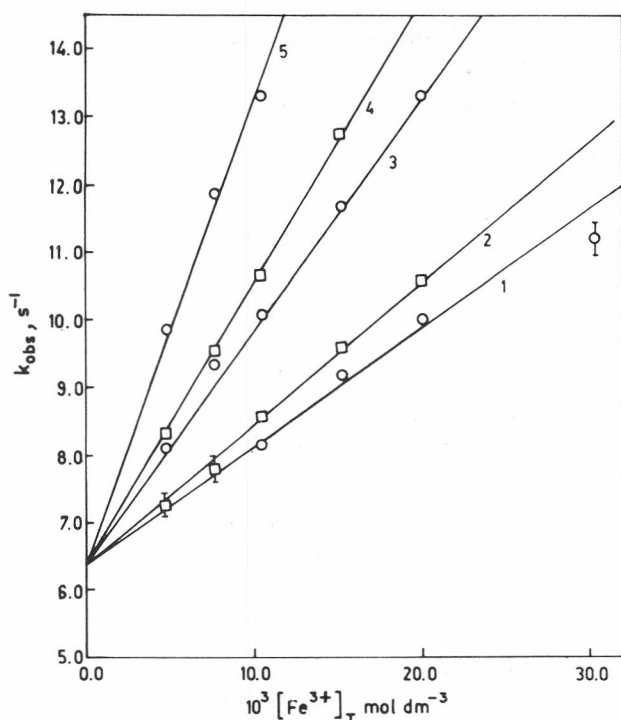
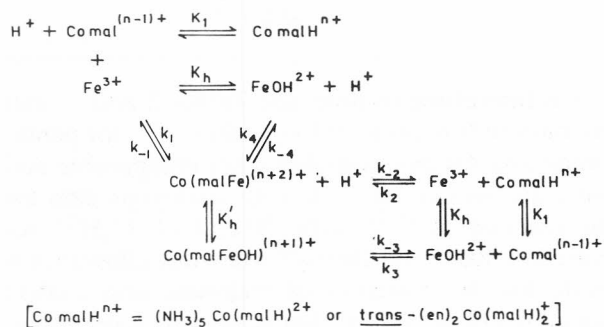


Fig. 1— k_{obs} versus $10^3 [\text{Fe}^{3+}]_{\text{T}}$ plot at 25°C (1, 2, 3, 4 and 5 for $[\text{H}^+] = 0.3, 0.2, 0.1, 0.075$ and 0.05 mol dm^{-3} , respectively)

indicative of the fact that only (1 : 1) binuclear complex is formed between Fe(III) and either of the substrates.

The possible reaction mechanism consistent with observed facts can be delineated as in Scheme 1.



Scheme 1

where,

$$k_{\text{obs}} = k_{\text{f}} f_1 f_2 [\text{Fe}^{3+}]_{\text{T}} + k_{\text{r}} f_3 \quad \dots (1)$$

$$k_{\text{f}} = (k_1 K_1 + k_4 K_h) [\text{H}^+]^{-1} + k_2 + k_3 K_1 K_h [\text{H}^+]^{-2} \quad \dots (2)$$

$$k_{\text{r}} = (k_{-1} + k_{-4}) + k_{-2} [\text{H}^+] + k_{-3} K_h' [\text{H}^+]^{-1} \quad \dots (3)$$

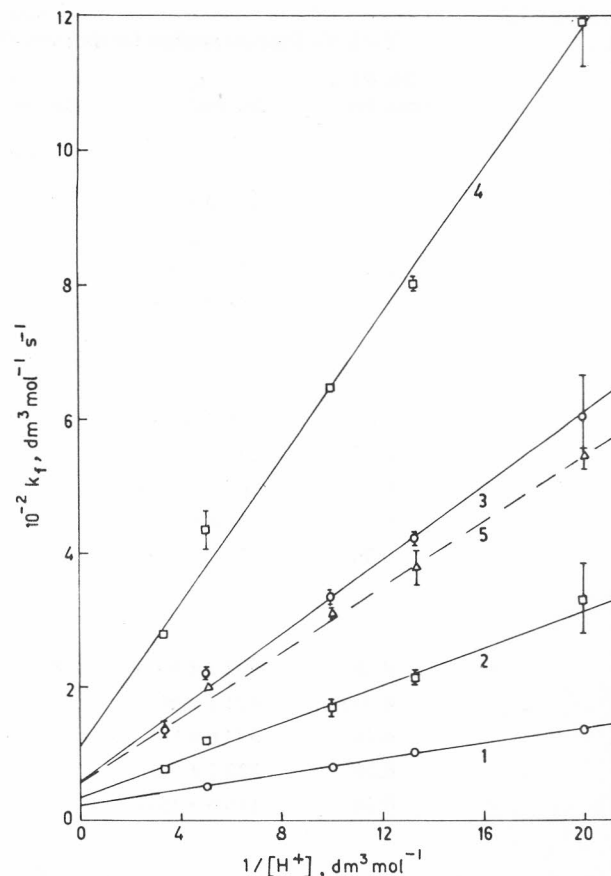


Fig. 2— $10^{-2} k_{\text{f}}$ versus $1/[\text{H}^+]$ plot (1, 2, 3 and 4 for *trans*-[Co(en)₂(malH)₂]⁺; 5 for [(NH₃)₅Co(malH)]²⁺)

$$f_1 = [\text{H}^+] / ([\text{H}^+] + k_h) \quad \dots (4)$$

$$f_2 = [\text{H}^+] / ([\text{H}^+] + K_1) \quad \dots (5)$$

$$f_3 = [\text{H}^+] / ([\text{H}^+] + K_h') \quad \dots (6)$$

Values of K_h were obtained from literature¹³⁺. The values $10^4 K_1$ for (NH₃)₅Co(malH)²⁺ and (en)₂Co(malH)₂⁺ at 30°C are 2.88 and 5.01, respectively. Values of K_h' are not known, nor they can be derived from our data. However, it can be assumed to be somewhat smaller than K_h (ref. 10). With the use of these values it follows that f_1, f_2, f_3 are reduced to unity in the acidity range used. k_{f} and k_{r} calculated from least squares slopes and intercepts of k_{obs} versus $[\text{Fe}^{3+}]_{\text{T}}$ plots are given in Tables 2 and 3. The inverse acidity dependence of k_{f} and no deviation from the linearity of the plots in Fig. 2 suggest

¹³The values of the hydrolysis constant of $\text{Fe}(\text{OH}_2)_6^{3+}$ (K_h) (1.48×10^{-3} and $2.44 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$ at 20 and 30°C and $I = 0.5 \text{ mol dm}^{-3}$ respectively) were obtained by intrapolation of literature data, K_h is 1.18×10^{-3} , 1.90×10^{-3} and 3.2×10^{-3} at 15, 25 and 35°C respectively, ($I = 0.5 \text{ mol dm}^{-3}$)¹³. With use of these values it can readily be shown that $[\text{H}^+]$ of the reaction medium as adjusted by added HClO_4 is changed only negligibly by the hydrolysis of $\text{Fe}(\text{OH}_2)_6^{3+}$.

Table 3—Rate parameters for the formation of *trans*-[Co(en)₂(malH)malFe]³⁺ species

[HClO ₄] _T (mol dm ⁻³)	k _r (dm ³ mol ⁻¹ s ⁻¹)	k ₂ (dm ³ mol ⁻¹ s ⁻¹)	10 ⁻³ k ₄ (dm ³ mol ⁻¹ s ⁻¹)	k _r (s ⁻¹)
15.0 ± 0.1°C				
0.05	136.0 ± 3.5	21.4 ± 4.2	5.00 ± 0.35	2.24 ± 0.03
0.075	105.5 ± 2.3	—	—	2.37 ± 0.02
0.10	78.3 ± 1.8	—	—	2.37 ± 0.02
0.20	50.7 ± 1.5	—	—	2.36 ± 0.02
20.0 ± 0.1°C				
0.05	330.0 ± 50.0	43.5 ± 12.7	8.97 ± 1.38	3.84 ± 0.44
0.075	215.0 ± 12.0	—	—	3.79 ± 0.14
0.10	167.0 ± 13.0	—	—	3.95 ± 0.18
0.20	119.0 ± 4.0	—	—	3.60 ± 0.06
0.30	75.0 ± 6.0	—	—	3.78 ± 0.15
25.0 ± 0.1°C				
0.05	603.0 ± 67.0	86.3 ± 17.2	13.22 ± 1.02	7.07 ± 0.52
0.075	421.1 ± 10.5	—	—	6.29 ± 0.09
0.10	334.0 ± 8.0	—	—	6.60 ± 0.12
0.20	222.2 ± 7.0	—	—	6.19 ± 0.09
0.30	136.0 ± 15.0	—	—	7.08 ± 0.34
30.0 ± 0.1°C				
0.05	119.2 ± 80.0	109.0 ± 15.0	21.77 ± 0.72	10.71 ± 0.58
0.075	800.6 ± 11.5	—	—	11.00 ± 0.16
0.10	645.8 ± 5.8	—	—	10.36 ± 0.08
0.20	435.0 ± 32.0	—	—	11.08 ± 0.42
0.30	281.0 ± 7.0	—	—	11.31 ± 0.11

that the last term in Eq. (2) is insignificant and can be neglected. The values of k_2 were derived from the intercepts of least squares plots of k_r versus $[H^+]^{-1}$ (Eq. 2). The slopes of such plots are equal to $(k_1K_1 + k_4K_h)$. However, in the acidity range used in this study both the cobalt(III) substrates will exist practically (>99.8%) in their undissociated acid forms ($pK = 3.54$ for $(NH_3)_5CoO_2CCH_2CO_2H^{2+}$ at $I = 0.3$ mol dm⁻³, temp. = 25°C; and $pK_1 = 3.30 \pm 0.01$, $pK_2 = 4.0 \pm 0.02$ for *trans*-(en)₂Co(O₂CCH₂CO₂H)₂⁺ at $I = 0.1$ mol dm⁻³ and temp. = 30°C). Hence k_1 -path is likely to be insignificant. Neglecting this path the slope of k_r versus $[H^+]^{-1}$ plot equals k_4K_h from which k_4 is calculated. Since k_r is independent of $[H^+]$ or $[H^+]^{-1}$, it is reasonable to assume that acid dependent paths (k_{-2} and k_{-3}) do not contribute significantly to the overall dissociation rate (see Eq. 3). Thus (k_{-4}) is identified with k_r . The associated activation parameters for various paths are collected in Table 4.

It is interesting to note (see Tables 2 and 3) that the rates of formation of $Co(malFe)^{n+21+}$ for pentamine and bis(en)₂ complexes are comparable and these are also comparable with analogous data for the reaction of Fe^{3+} with $(NH_3)_5CoC_2O_4H^{2+}$ reported by Dash and Harris¹⁰ when due allowance is made for the basicities of malonate and oxalate bound to cobalt(III). Further the electrostatic repulsion between the interacting like-charge cations (Co^{III} and Fe^{III}) is likely to be less for the Hmalonato complex than that for corresponding oxalato complex. This is compatible with observed rate of anation of $Fe(OH_2)_5OH^{2+}$ by $Hmal^-$ ($k = 13 \times 10^4$ dm³ mol⁻¹ s⁻¹ at 25°C; see ref. 14). Presumably this is one of the reasons why reaction path k_2 was observed for the malonato complex (the analogous path for the reaction of $(NH_3)_5CoC_2O_4H^{2+}$ with $Fe(OH_2)_6^{3+}$ was, however, not observed). The present view on the ligand substitution reactions at $Fe(III)$ centres is that I_a and I_d mechanisms operate

Table 4—Rates and activation parameters for binuclear complexation reactions $(\text{NH}_3)_5\text{Co}(\text{malH})^{2+}$ and $\text{trans}[\text{Co}(\text{en})_2(\text{malH})_2]^+$ with Fe^{3+} , $I = 0.5 \text{ mol dm}^{-3}$

		ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)
$k_2, \text{s}^{-1} \text{ dm}^3 \text{ mol}^{-1}$	86.2 ± 17.2 (71.1 ± 13.9) small*	75.8 ± 10.4	44.4 ± 39.94
$10^{-4} k_4, \text{s}^{-1} \text{ dm}^3 \text{ mol}^{-1}$	1.32 ± 0.21 (1.26 ± 0.10) 0.46*	68.5 ± 1.53	31.2 ± 5.1
k_{-4}, s^{-1a}	6.64 ± 0.42 (5.11 ± 0.20) 0.5*	72.2 ± 1.73	12.8 ± 5.9

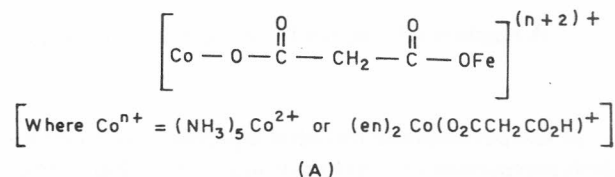
^aAt $25.0 \pm 1^\circ\text{C}$, Values in parentheses are for $(\text{NH}_3)_5\text{Co}(\text{malH})^{2+}$ and all others are for $\text{trans}[\text{Co}(\text{en})_2(\text{malH})_2]^+$

*Analogous data for the oxalatopentaammine ion at 25°C , $I = 1.0 \text{ mol dm}^{-3}$

for $\text{Fe}(\text{OH}_2)_6^{3+}$ and $\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$ respectively^{10,15}. The values of outersphere association constant, K_{os} , for the substrates under consideration cannot be greater than unity considering the electrostatic effect¹⁶. In this context, it is worth noting that the values of k_2^* and k_4^* for both the substrates ($k_2^* \approx 80 \pm 20 \text{ s}^{-1}$ and $k_4^* \approx (1.3 \pm 0.50) \times 10^4 \text{ s}^{-1}$)[†] at 25°C are lower than the values of water exchange rate constant of iron(III) species ($k_{\text{ex}}^{25^\circ\text{C}} = 1.6 \times 10^2 \text{ s}^{-1}$ and $1.4 \times 10^5 \text{ s}^{-1}$ for $\text{Fe}(\text{OH}_2)_6^{3+}$ and $\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$ respectively¹⁴). Hence water dissociation from Fe(III) centre is more likely to be rate-controlling for the formation of binuclear complex at least for $\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$. However, compared to $\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$, the mechanism of substitution reaction at $\text{Fe}(\text{OH}_2)_6^{3+}$ centre is more likely to be I_a as also suggested in the case of formation of binuclear complex of iron(III) with several salicylatopentaamine cobalt(III) complexes¹¹.

The rate constants for the spontaneous dissociation path (k_{-4}) for both the cobalt(III) substrates are comparable and are ~ 10 times higher than that for $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Fe}^{4+}$. However, in comparison to Fe(III)-monochloroacetate^{10,18} ($k_{-4} \approx 20 \text{ s}^{-1}$) the Fe(III)-malonate species under consideration dissociates nearly four-times slower. These differences are not large enough considering the complexity of the reactions. It, however, might indicate that the binuclear species of the malonate complexes, are more prone to exist in the non-chelated form (A)

[†]It is generally accepted^{15,17} that the derived second-order rate constants, k in substitutions of this type are a combination of rapid outer sphere precursor complex formation with equilibrium constant K_{os} , and a rate constant for dissociative water elimination such that $k = k^* K_{\text{os}}$ for small values of K_{os} .



The activation enthalpies and entropies (see Table 4) for the formation and dissociation of the binuclear species are almost alike and fall in the range expected for similar other substitution reactions of Fe(III) using conventional ligands.

Acknowledgement

We are thankful to Prof A C Dash for many helpful discussions. ND thanks the CSIR, New Delhi for the award of a senior research fellowship.

References

- 1 Dash A C & Nanda R K, *Inorg Chem*, 13 (1974) 655.
- 2 Dash A C & Nanda R K, *J Indian chem Soc*, 52 (1975) 289.
- 3 Dash A C & Nanda R K, *J inorg nucl chem*, 37 (1975) 2139.
- 4 Dash A C, *J inorg nucl Chem*, 40 (1978) 132.
- 5 Dash A C & Nanda R K, *Inorg Chem*, 12 (1975) 2024.
- 6 Nanda R K & Dash A C, *J inorg nucl Chem*, 36 (1974) 1595.
- 7 Dash A C, Khatoun S & Nanda R K, *Indian J Chem*, 23A (1984) 997.
- 8 Das N N & Nanda R K, *Indian J Chem*, 28A (1989) 26.
- 9 Das N N & Nanda R K, *Transition Met Chem*, 15 (1990) 293.
- 10 Dash A C & Harris G M, *Inorg Chem*, 21 (1982) 1265.
- 11 Dash A C & Harris G M, *Inorg Chem*, 21 (1982) 2336.
- 12 Dash A C, *Inorg Chem*, 22 (1983) 837.
- 13 Connick R E, Hepler L G, Huges Z Z, Kury Jr. J W, Latimar W M & Taso M S, *J Am chem Soc*, 78 (1956) 1827.
- 14 Cavasino F P & Di Dio E, *J chem Soc (A)*, (1971) 3176.
- 15 Grant M & Jordan R B, *Inorg Chem*, 20 (1981) 55.
- 16 Hammes G G & Steinfield J I, *J Am chem Soc*, 84 (1962) 4639.
- 17 Gouger S & Stuehr J, *Inorg Chem*, 13 (1974) 379.
- 18 Perlmutter Hayman B & Tapuhi E, *J coord Chem*, 6 (1976) 31.