

Stability Constants of the Binuclear Species of Iron(III) with Pentaammine-(substituted salicylato)cobalt(III) Complexes

Anadi C. Dash,^A Rabindra K. Nanda^A and Himansu K. Patnaik^{A,B}

^A Department of Chemistry, Utkal University, Bhubaneswar-4, India.

^B Chemistry Department, B.J.B. College, Bhubaneswar-6, India.

Abstract

The stability constants of the binuclear species of iron(III) with some pentaammine(substituted salicylato)cobalt(III) complexes have been measured spectrophotometrically. At 28°C and $\mu = 0.6M$ the values of the stability constants of the species $(NH_3)_5Co\{CO_2C_6H_3(X)O\}Fe^{4+}$ are found to be $4.22(\pm 0.38) \times 10^{10}$ l. mol⁻¹ (X = 5-SO₃⁻), $5.29(\pm 0.79) \times 10^{10}$ l. mol⁻¹ (X = 5-Br) and $4.39(\pm 0.54) \times 10^9$ l. mol⁻¹ (X = 5-NO₂). Both pK_{OH} of the cobalt(III) substrates and the stability constants of the binuclear species are found to decrease in the order 5-Br > 5-SO₃⁻ > 5-NO₂.

The equilibria involving pentaamminesalicylatocobalt(III) and metal ions such as iron(III), aluminium(III) and gallium(III) have been studied earlier¹ in this Laboratory. This paper describes the study of the equilibria involving iron(III) and some pentaammine(substituted salicylato)cobalt(III) complexes in aqueous media. The purpose was to find how substitution in the salicylato moiety affects the stabilities of the binuclear complexes, $(NH_3)_5Co\{CO_2C_6H_3(X)O\}Fe^{4+}$.

Experimental

$[(NH_3)_5Co\{CO_2C_6H_3(X)OH\}](ClO_4)_2$, the pentaammine(substituted salicylato)cobalt(III) perchlorates, were prepared by the method of Gould and Taube² and purified by repeated crystallization from aqueous perchloric acid solutions. The samples were dried over fused calcium chloride at room temperature. The purity of the samples was checked by estimating Co content of each complex. The spectral and analytical data for the complexes have been collected in Table 1.

Table 1. Analytical and spectral data

Complex	Cobalt (%)		λ_{max} (nm)	ϵ_{max} (l. mol ⁻¹ cm ⁻¹)
	Calc.	Found		
$[(NH_3)_5Co\{CO_2C_6H_3(5-SO_3)OH\}](ClO_4)_2$	12.8	12.7	515	79.5
$[(NH_3)_5Co\{CO_2C_6H_3(5-Br)OH\}](ClO_4)_2$	10.5	10.4	510	82.7
$[(NH_3)_5Co\{CO_2C_6H_3(5-NO_2)OH\}](ClO_4)_2$	11.2	11.1	510	80.7

Ferric perchlorate was prepared from $FeCl_3 \cdot 6H_2O$ (A.R.) and perchloric acid (A.R.). The free acid and iron(III) contents of the stock solution of $Fe(ClO_4)_3$ were estimated by standard procedures.³

¹ Dash, A. C., and Nanda, R. K., *Inorg. Chem.*, 1973, 12, 2024.

² Gould, E. S., and Taube, H., *J. Amer. Chem. Soc.*, 1964, 86, 1318.

³ Vogel, A. I., 'A Text Book of Quantitative Inorganic Analysis' 3rd Edn (Longmans: London 1961).

B.D.H. reagent grade sodium perchlorate and perchloric acid (A.R.) were used to adjust ionic strength and acidity of the reaction medium. All solutions were prepared in distilled water. Optical density measurements were made with a Beckman DU₂ spectrophotometer using 1-cm matched silica cells. Distilled water was taken to be the 100% transmission standard.

Equilibrium Constant Measurements

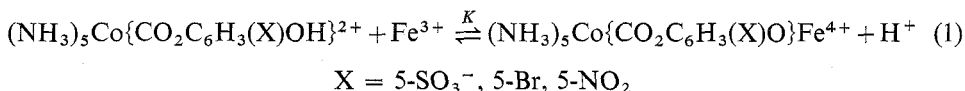
Requisite amounts of sodium perchlorate, perchloric acid and ferric perchlorate solutions were mixed in 10 ml volumetric flasks. A known volume of a freshly prepared solution of the complex was then transferred into the reaction flask. The optical densities of the reaction mixture were measured immediately after mixing. Absorbances of the reaction mixtures did not change with time during the course of measurement. This indicated that the equilibrium between the complex and ferric ion is rapidly established and that the former does not undergo metal-ion catalysed hydrolysis during the time of measurement.

The dissociation constants of the phenolic group of the three complexes at room temperature (28°C) were determined from the measured optical densities of the complex solutions in a series of carbonate-bicarbonate buffers at suitable wavelengths and at $\mu = 0.6M$.

Calculations and Results

Equilibrium Constant

The equilibrium in solutions containing iron(III) perchlorate and pentaammine(substituted salicylato)cobalt(III) ions may be represented as



If d_1 and d_2 are optical densities of solutions of the complex alone and mixed respectively, and ϵ_1 and ϵ_2 are extinction coefficients of $(NH_3)_5Co\{CO_2C_6H_3(X)OH\}^{2+}$ and $(NH_3)_5Co\{CO_2C_6H_3(X)O\}Fe^{4+}$ respectively, then it is possible to derive the relationship:

$$C_1/(d_2 - d_1) = 1/(\epsilon_2 - \epsilon_1)l + \{1/(\epsilon_2 - \epsilon_1)lK\}[H^+]/C_2 \quad (2)$$

where

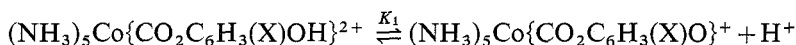
$$C_1 = [(NH_3)_5Co\{CO_2C_6H_3(X)OH\}^{2+}] \quad C_2 = [Fe^{3+}]_{free} = [Fe^{3+}]_{total}$$

(decrease of iron(III) concentration due to the formation of the binuclear species is neglected); l , cell path length; K defined by equation (1).

A least-squares computer program for equation (2) was adopted to calculate the best values of the slope and intercept of plots of $C_1/(d_2 - d_1)$ against $[H^+]/C_2$. The values of K were computed from the least-squares best values of the slopes and intercept of such plots. Relevant data have been summarized in Tables 2 and 3.

pK_{OH} Values

The acid dissociation equilibrium of the complexes may be represented as



For such a system, it can be shown that

$$a/(D - D_0) = 1/(\epsilon_2 - \epsilon_1)l + [1/(\epsilon_2 - \epsilon_1)lK_1]K_a(HCO_3^-)[HCO_3^-]/[CO_3^{2-}]$$

where ϵ_1 and ϵ_2 are the extinction coefficients of protonated and deprotonated species respectively; D and D_0 are the optical density of the complex of a given concentration

a in bicarbonate-carbonate buffer and in 0.1M HClO_4 medium respectively and $K_a(\text{HCO}_3^-)$ is the dissociation constant of bicarbonate ion. K_1 was calculated from the least squares intercept and plots of $a/(D-D_0)$ against $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$. The value of $K_a(\text{HCO}_3^-)$ was taken to be 4.8×10^{-11} , $\mu = 0.0\text{M}$, at 25°C .⁴ The values of $\text{p}K_{\text{OH}}$ of the complexes at 28°C and $\mu = 0.6\text{M}$ were found to be 9.69 ± 0.04 ($\text{X} = 5\text{-SO}_3^-$), 9.83 ± 0.06 ($\text{X} = 5\text{-Br}$) and 8.81 ± 0.04 ($\text{X} = 5\text{-NO}_2$).

Table 2. Equilibrium data for reaction (1) at 28°C
 $10^4 \times [\text{complex}]$: 5.27 mol l^{-1} ($\text{X} = 5\text{-SO}_3^-$); 5.02 mol l^{-1}
 ($\text{X} = 5\text{-Br}, 5\text{-NO}_2$)

$10^3 \times [\text{Fe}^{3+}]$ (mol l^{-1})	$[\text{H}^+]$ (mol l^{-1})	Optical density at 540 nm		
		5-SO_3^-	5-Br	5-NO_2
0.0	0.05	0.028	0.031	0.029
2.0	0.05	0.250	0.218	0.199
4.0	0.05	0.403	0.316	0.309
8.0	0.05	0.552	0.451	0.463
10.0	0.05	0.600	0.510	0.515
15.0	0.05	0.671	0.585	0.595
20.0	0.05	0.726	0.650	0.655
10.0	0.10	0.437	0.375	0.295
10.0	0.20	0.304	0.245	0.195
10.0	0.30	0.230	0.191	0.145

Table 3. K values for reaction (1) at 28°C
 $\mu, 0.6\text{M}$; $l, 1 \text{ cm}$

	5-SO_3^-	5-Br	5-NO_2
$10^4 [1/(\epsilon_2 - \epsilon_1)/l]$	5.79 ± 0.15	6.43 ± 0.23	5.99 ± 0.41
$10^5 [1/K(\epsilon_2 - \epsilon_1)l]$	6.80 ± 0.10	8.32 ± 0.13	8.92 ± 0.26
K	8.52 ± 0.26	7.72 ± 0.31	6.72 ± 0.50

Discussion

From the known values of K and the acid dissociation constant (K_1) of the substituted salicylato complexes, the stability constants of the binuclear complexes of iron(III) ($K_{\text{stab}} = K/K_1$) have been calculated to be $7.44(\pm 0.29) \times 10^{10}$,¹ $4.22(\pm 0.38) \times 10^{10}$, $5.29(\pm 0.79) \times 10^{10}$ and $4.39(\pm 0.54) \times 10^9 \text{ l. mol}^{-1}$ for the complexes $(\text{NH}_3)_5\text{-Co}\{\text{CO}_2\text{C}_6\text{H}_3(\text{X})\text{O}\}\text{Fe}^{4+}$ where $\text{X} = \text{H}, 5\text{-SO}_3^-, 5\text{-Br}$ and 5-NO_2 respectively.

The stability constant data reveal that iron(III) complexes of the salicylate dianions^{5,6} are thermodynamically about 10^5 times more stable than their pentaammine cobalt(III) analogues. This result indicates that the effect of coordination on the complexing ability of salicylates is considerable. Furthermore the $\text{p}K_{\text{OH}}$ values of the pentaammine salicylates and the stability constants of their iron(III) complexes decrease in the order: $5\text{-Br} > 5\text{-SO}_2^- > 5\text{-NO}_2$. Thus it is evident that the proton affinity of $(\text{NH}_3)_5\text{Co}\{\text{CO}_2\text{C}_6\text{H}_3(\text{X})\text{O}\}^+$ species parallels their complexing ability towards iron(III).

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⁴ Nakayama, F. S., *J. Inorg. Nucl. Chem.*, 1971, **33**, 1287.

⁵ Ernst, Z. L., and Menashi, J., *Trans. Faraday Soc.*, 1963, **59**, 2838.

⁶ Ogawa, K., and Tobe, N., *Bull. Chem. Soc. Jap.*, 1966, **39**, 223.