Stability of Metal Chelates of Co(II), Ni(II), Mn(II) and Zn(II) with 7-Iodo-8-hydroxyquinoline-5-sulphonic Acid (Ferron)

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The interaction of Co(II), Ni(II), Mn(II), and Zn(II) ions with 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) was investigated by potentiometric titration. Stability constants of the 1:1 and 2:1 chelates of all four metals, and the 3:1 chelates of the hexa-coördinated ions Co(II) and Ni(II) were calculated on the basis of titrations with standard alkali of mixtures of the ligand and metal ion. A comparison of the stability constants of the ferron complexes with those of the 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulphonic acid complexes showed a decreasing stability following the same order as the decreasing basicity of the ligands.

In connection with earlier investigations of the interaction of 7-iodo-8-hydroxyquinoline-5-sulphonic acid with aluminium¹ and ferric iron², it was considered of interest to study the complexes formed between ferron and the metal ions Co(II), Ni(II), Mn(II), and Zn(II). The stability of the calcium and magnesium complexes was previously determined by Ekman and Näsänen³ and Engan⁴, respectively.

The interactions between metal and ligand were studied under conditions such that the maximum coördination number of the metal ion was obtained.

EXPERIMENTAL

Methods. The experimental method consisted of potentiometric titration of different mixtures of ferron and metal ion. The ionic strength was kept relatively constant by maintaining a concentration of 0.10 M potassium chloride and by keeping a low concentration of ligand and metal ion. The titrations were carried out in a thermostated, double-walled titration vessel, and the temperature was kept at 25.0 ± 0.1 C.

Instruments. The Beckman Zeromatic pH meter (glass and calomel reference electrodes) was used to determine the hydrogen ion concentrations. It was calibrated against the Beckman Buffer solution and a 0.05 M potassium hydrogenphthalate solution. The temperature was maintained constant by an ultrathermostat.

Reagents. All chemicals used were of reagent grade quality. The stock solutions of the metal ions were standardized by complexometric titrations with a standard solution of the disodium salt of ethylenediaminetetraacetic acid in the presence of suitable indicators.

The concentrations of the standard solutions were all approximately 5×10^{-3} M.

For each metal equimolar solutions of ferron were prepared by accurate weighing.

A 0.0825 N solution of potassium hydroxide was used for the titrations.

Procedure. Solutions containing 1:1, 2:1, and 3:1 molar ratios of ligand to metal ion were prepared by pipetting 25 ml of the metal solution into the titration vessel and adding 25, 50, or 75 ml of the ferron solution. After thermal equilibrium was reached, standard alkali was added in small increments and the corresponding pH data were recorded as soon as constant values were obtained.

CALCULATIONS

Acid dissociation constants of ferron. The values determined previously¹ were employed in this investigation ($pK_1 = 2.50$ and $pK_2 = 7.11$ at $25.0 \pm 0.1^\circ\text{C}$ and in the presence of 0.10 M potassium chloride).

Stability constants. The stability constants of the complexes were calculated according to the method originally described by Bjerrum⁵.

The expression for calculating $[A^{2-}]$ is:

$$[A^{2-}] = \frac{(2-a)C_A - [H^+] + [OH^-]}{\frac{2[H^+]}{K_1 \cdot K_2} + \frac{[H^+]}{K_2}}$$

where a represents the number of moles of base added per mole of ligand, C_A the total concentration of ligand species and K_1 and K_2 are the acid dissociation constants of ferron. The average number of moles of ligand bound per mole of metal ion, the formation function, is designated by $\bar{n}$ and was calculated from the expression:†

$$\bar{n} = \frac{C_A - \left(\frac{[H^+]^2}{K_1 \cdot K_2} + \frac{[H^+]}{K_2} + 1 \right) [A^{2-}]}{C_M}$$

where C_M represents the total concentration of the metal species.

Values of pA , the negative logarithm of $[A^{2-}]$, were plotted against $\bar{n}$. The values of pA at $\bar{n} = 0.5, 1.5$, and 2.5 were taken as $\log K_{MA}$, $\log K_{MA}$, and $\log K_{MA}$, respectively.

RESULTS

Cobalt. Titration of the 1:1 mixture of ligand and cobalt(II) ion (Fig. 1) resulted in a steep inflection at $m = 2$ (m represents the number of moles of base added per mole of metal). The reaction taking place was believed to be:

Precipitation of what appeared to be cobaltous hydroxide began at a pH value of approximately 10.

Fig. 1. Potentiometric titration of 1:1, 2:1, and 3:1 molar ratios of 7-iodo-8-hydroxyquinoline-5-sulphonic acid and cobalt(II). m = moles of base added per mole of metal.

Fig. 2. Potentiometric titration of 1:1, 2:1, and 3:1 molar ratios of 7-iodo-8-hydroxyquinoline-5-sulphonic acid and nickel(II). m = moles of base added per mole of metal.

A steep inflection at $m = 4$ appeared on the 2:1 titration curve, corresponding to the reaction:

but no precipitate was observed during the titration.

Titration of the 3:1 mixture resulted in an inflection at $m = 6$, probably corresponding to the reaction:

Fig. 3. Potentiometric titration of 1:1 and 2:1 molar ratios of 7-iodo-8-hydroxyquinoline-5-sulphonic acid and manganese(II). m = moles of base added per mole of metal.

Fig. 4. Potentiometric titration of 1:1 and 2:1 molar ratios of 7-iodo-8-hydroxyquinoline-5-sulphonic acid and zinc(II). m = moles of base added per mole of metal.

No precipitate was observed at any time during the titration. The lack of a steep inflection of the 3:1 titration curve indicated only a slight affinity of the metal ion for the donor groups of the third ligand molecule.

No indications of hydroxo chelate formation, as for the aluminium¹ and ferric iron² ions, were apparent in any of the titrations of the cobalt(II) chelates. The precipitation of the 1:1 mixture seemed to be due to disproportionation to the 2:1 chelate and cobaltous hydroxide.

Nickel. Titration of the 1:1, 2:1, and 3:1 mixtures of ligand per mole nickel(II) ion (Fig. 2), resulted in inflections at $m = 2, 4$, and 6 , corresponding to the reactions given for the cobalt(II) chelates, and the formation of the chelates NiA , NiA_2^{2-} and NiA_3^{4-} , respectively. Precipitation was seen in the 1:1 mixture above approximately pH 9, probably due to the disproportionation of the 1:1 chelate to the 2:1 chelate and nickelous hydroxide. The nickel(II) ion showed also only a slight affinity for the donor groups of the third ligand molecule. No indication of hydroxo chelate formation was apparent.

Manganese. Titration of equimolar amounts of ligand and Mn(II) ion gave a single inflection after addition of two moles of base per mole of metal (Fig. 3), corresponding to the reaction:

Precipitation occurred at a pH value of approximately 7.0, probably due to the disproportionation of the chelate and precipitation of manganese hydroxide.

Titration of the 2:1 mixture resulted in an inflection at $m = 4$, corresponding to the reaction:

Precipitation of manganese hydroxide occurred at approximately pH 10.

Zinc. Titration of solutions containing the 1:1 and 2:1 Zn(II) chelates, resulted in steep inflections at $m = 2$ and 4 (Fig. 4), due to the formation of AZn and ZnA_2^{2-} . In the 1:1 mixture precipitation took place from approxi-

Fig. 5. Formation curves of the chelates of 7-iodo-8-hydroxyquinoline-5-sulphonic acid with Co(II), Ni(II), Mn(II), and Zn(II).

Table 1. Stability constants of Co(II), Ni(II), Mn(II), and Zn(II) ions with 7-iodo-8-hydroxyquinoline-5-sulphonic acid.

M^{n+}	$\log K_1$	$\log K_2$	$\log K_3$
Co^{2+}	7.3	6.3	5.0
Ni^{2+}	8.2	7.0	5.6
Mn^{2+}	5.3	4.3	
Zn^{2+}	7.1	6.1	

$t = 25.0 \pm 0.1^\circ C$; $\mu = 0.10$

Acid dissociation constants: $pK_1 = 2.50$; $pK_2 = 7.11$

Table 2. Stability constants of Co(II), Ni(II), Mn(II), and Zn(II) ions with 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulphonic acid and 7-iodo-8-hydroxyquinoline-5-sulphonic acid.

M^{n+}	8-Hydroxyquinoline		8-Hydroxyquinoline-5-sulphonic acid			7-Iodo-8-hydroxyquinoline-5-sulphonic acid		
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_1$	$\log K_2$	$\log K_3$
Co^{2+}	10.91	9.9	8.11	6.95	5.36	7.3	6.3	5.0
Ni^{2+}	11.65	10.4	9.02	7.75	6.16	8.2	7.0	5.6
Mn^{2+}			5.67	5.05		5.3	4.3	
Zn^{2+}	10.91	9.9	7.54	6.78		7.1	6.1	

Table 3. Comparison of the stability constants of Co(II), Ni(II), Mn(II), and Zn(II) ions with 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulphonic acid and 7-iodo-8-hydroxyquinoline-5-sulphonic acid.

M^{n+}	8-Hydroxyquinoline and 8-hydroxyquinoline-5-sulphonic acid		8-Hydroxyquinoline and 7-iodo-8-hydroxyquinoline-5-sulphonic acid		8-Hydroxyquinoline-5-sulphonic acid and 7-iodo-8-hydroxyquinoline-5-sulphonic acid		
	$\Delta \log K_1$	$\Delta \log K_2$	$\Delta \log K_1$	$\Delta \log K_2$	$\Delta \log K_1$	$\Delta \log K_2$	$\Delta \log K_3$
Co^{2+}	2.8	3.0	3.6	3.6	0.81	0.65	0.36
Ni^{2+}	2.6	2.6	3.4	3.4	0.82	0.75	0.56
Mn^{2+}					0.37	0.75	
Zn^{2+}	3.4	3.1	3.8	3.8	0.44	0.68	

mately pH 7.5, but in the 2:1 solution no precipitate was observed during the titration.

Stability constants and discussion. The Bjerrum formation functions for the cobalt(II), nickel(II), manganese(II), and zinc(II) chelates were calculated from the titration curves and are plotted in Fig. 5. The stability constants are listed in Table 1.

In Table 2 the relative stabilities of the Co(II), Ni(II), Mn(II), and Ni(II) chelates of 7-iodo-8-hydroxyquinoline-5-sulphonic acid are compared with the stabilities of corresponding 8-hydroxyquinoline-5-sulphonic acid complexes reported by Richard *et al.*⁶ and of 8-hydroxyquinoline complexes reported by Irving⁷. The lower basicity of the ligand when going from 8-hydroxyquinoline to ferron is reflected in a lower stability of the metal chelates.

A comparison of the relative stabilities of the chelates is made in Table 3. The differences between $\log K$ for corresponding chelates are in good agreement. The average $\Delta \log K_1$ and $\Delta \log K_2$ between the chelates with 8-hydroxyquinoline and with ferron are both 3.6, and between 8-hydroxyquinoline-5-sulphonic acid and ferron the average $\Delta \log K_1$, $\Delta \log K_2$, and $\Delta \log K_3$ are 0.6, 0.7, and 0.5, respectively. There seems to be a difference between $\Delta \log K_1$ for the hexacoordinated Co(II) and Ni(II) ions and $\Delta \log K_1$ for Mn(II) and Zn(II) ions, but the data are insufficient to allow any conclusion.

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