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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF PITTSBURGH, PITTSBURGH 13,
PENNSYLVANIA

Stabilities of Divalent Metal Complexes of Certain Substituted 4-Hydroxybenzothiazoles

BY PAO KUO FENG[1] AND QUINTUS FERNANDO[2]

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Formation constants of the chelates of 4-hydroxybenzothiazole-7-sulfonic acid with several divalent metal ions are compared with the corresponding formation constants of the chelates of 4-hydroxybenzothiazole[3] and of 2-amino-4-hydroxybenzothiazole.[4] The formation constants of the chelates of the latter compound that have been reported recently have been independently confirmed in this work.

Experimental

Preparation of Compounds.—A detailed description of the preparation of 4-hydroxybenzothiazole has been published in an earlier paper.[3] 5,7-Dibromo-4-hydroxybenzothiazole was prepared by adding an aqueous solution containing 15 g. of potassium bromide and 10 g. of bromine slowly and with vigorous stirring to a solution containing 1 g. of 4-hydroxybenzothiazole in ethanol until the solution acquired a yellow color. Fifty ml. of water was added and the mixture stirred vigorously. The compound formed was filtered, washed with a dilute solution of sodium bisulfite, and recrystallized from an ethanol–water mixture; m.p. 202–203°, reported m.p. 203°.[5] *Anal.* Calcd. for $C_7H_3NOSBr_2$: N, 4.54. Found: N, 4.62.

4-Hydroxybenzothiazole-7-sulfonic acid[6] was prepared by dissolving 1 g. of 4-hydroxybenzothiazole in 40 g. of cold concentrated sulfuric acid and allowing the mixture to stand at room temperature for two days. The mixture then was poured into 150 ml. of water containing crushed ice. The compound formed was filtered and recrystallized from a mixture of hot water and concentrated hydrochloric acid. *Anal.* Calcd. for $C_7H_5NO_4S_2$: N, 6.06; S, 27.74. Found: N, 6.17; S, 28.02.

2-Amino-4-hydroxybenzothiazole was prepared by the demethylation of 2-amino-4-methoxybenzothiazole.[3,7] Twenty g. of 2-amino-4-methoxybenzothiazole was refluxed with 6 g. of red phosphorus, 100 ml. of hydriodic acid (density 1.7), and 20 ml. of glacial acetic acid for about 7 hr. Approximately 100 ml. of water was added to the hot solution and the red phosphorus was filtered immediately on a sintered glass funnel. A small amount of sodium bisulfite was added to the solution which then was neutralized with sodium carbonate. A colorless compound was formed, which was recrystallized from hot water; m.p. 182–184°. *Anal.* Calcd. for $C_7H_6N_2OS$: N, 16.86. Found: N, 16.23.

Acid Dissociation Constants.—The acid dissociation constants of the compounds were determined potentiometrically at 25 ± 0.1° in 50% v./v. dioxane–water. The experimental procedure has been described previously.[3]

The acid dissociation constants of 4-hydroxybenzothiazole-7-sulfonic acid were determined spectrophotometrically in water at 25°. A 5.29×10^{-5} M solution of the sulfonic acid in perchloric acid or a buffer solution containing acetate, borate, and phosphate ions, was used in the spectrophotometric method. Between *p*H 1 and 11, the ionic strength of the solution was kept constant at 0.1 by the addition of calculated quantities of sodium chloride. *p*H values of the solutions below 1.0 were calculated. All other *p*H values were measured with a Beckman Model G *p*H meter with a glass–saturated calomel electrode pair, calibrated with standard buffers at *p*H 4.00 and 7.00. All absorbance measurements were made with a Model 14 Cary recording spectrophotometer using matched 1-cm. silica cells. The absorbances of about twenty-five solutions were determined at 257, 275, and 247 mμ. The acid dissociation constants were calculated from the absorbance *vs.* *p*H data.

Chelate Formation Constants.—The Bjerrum[8] potentiometric method was used in this work. The experimental technique has been described previously.[3] The divalent metal chelates of 5,7-dibromo-4-hydroxybenzothiazole were quite insoluble in 50% v./v. dioxane–water and therefore it was impossible to obtain chelate formation constants in most cases by this potentiometric method. Although the chelates of 4-hydroxybenzothiazole-7-sulfonic acid were soluble in water, chelate formation constants with divalent metals were determined in 50% v./v. dioxane–water for purposes of comparison with the formation constants of analogous compounds that have been determined in 50% v./v. dioxane–water.

Potentiometric titrations were carried out with a metal: ligand ratio of 1:5. The values of log K_1 and log K_2 given in Table II are the average values obtained from two to three different titrations with each metal ion. The stepwise chelate formation constants K_1 and K_2 were deter-

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(1) Abstracted from a part of a Ph.D. thesis submitted by P. K. Feng to the Department of Chemistry, University of Pittsburgh.

(2) Department of Chemistry, University of Arizona, Tucson, Arizona.

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(4) T. J. Lane and A. Sam, *ibid.*, **83**, 2223 (1961).

(5) H. Erlenmeyer, *Helv. Chim. Acta*, **21**, 1695 (1938).

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(7) H. Erlenmeyer, H. Ueberwasser, and H. M. Weber, *ibid.*, **21**, 709 (1938).

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mined from a straight line obtained by plotting $(R^-)^2 \cdot (\bar{n} - 2)/\bar{n}$ vs. $(R^-)(\bar{n} - 1)/\bar{n}$, where (R^-) is the concentration of the anionic species of the ligand and $\bar{n}$ the average number of ligand molecules bound per metal ion. The slope and intercept of this line are equal to $1/K_2$ and $1/K_1K_2$, respectively.

Results and Discussion

The acid dissociation constants of the substituted 4-hydroxybenzothiazoles are given in Table I. The stepwise chelate formation constants K_1 and K_2 are collected in Table II. All equilibrium constants in this work are concentration quotients since activity coefficients have not been taken into account. If it is assumed that the error in the determination of the hydrogen ion concentration is far greater than all the other errors encountered in the Bjerrum potentiometric method, and if it also is assumed that the reliability of the measured pH is ±0.01, then the reliability of the log K_1 and log K_2 values that are reported in this work is approximately ±0.1.[9]

The over-all stability sequence for the metal complexes of 2-amino-4-hydroxybenzothiazole is Cu > Ni, Zn > Co > Mn. The position of zinc(II) in this series seems to be anomalous since the over-all formation constant for zinc(II) is greater than that of cobalt(II) and about the same as that of nickel(II). This increase in the stability of the zinc chelate with respect to that of the nickel chelate is not as great as with ligands such as 2-methyl-8-hydroxyquinoline, in which steric hindrance to chelate formation has been observed.[11]

TABLE I

ACID DISSOCIATION CONSTANTS OF SUBSTITUTED 4-HYDROXYBENZOTHIAZOLES AT 25°

	pK_{NH}	pK_{OH}
In aqueous solution		
4-Hydroxybenzothiazole[10]	1.2	8.85
4-Hydroxybenzothiazole-7-sulfonic acid	0.6	7.71
In 50% v./v. dioxane–water		
4-Hydroxybenzothiazole[3]	<2	10.75
2-Amino-4-hydroxybenzothiazole	3.86	11.69
5,7-Dibromo-4-hydroxybenzothiazole	<2	8.16
4-Hydroxybenzothiazole-7-sulfonic acid	<2	10.28

The stability order for the metal complexes of 4-hydroxybenzothiazole-7-sulfonic acid is Cu > Ni > Co > Zn > Mn, which is the usual order obtained for divalent metal complexes. The values of log K_1 for the copper, nickel, and cobalt chelates of the 7-sulfonic acid are higher than the corresponding values of log K_1 for 4-hydroxybenzothiazole; but the values of log K_2 for the sulfonic acid derivative are smaller than the corresponding log K_2 values for 4-hydroxybenzothiazole. This indicates that the uncharged 1:1 chelate of the sulfonic acid derivative is formed readily whereas it is more difficult to form the chelate with a metal:ligand ratio of 1:2, presumably due to the double negative charge on the anionic species of the ligand. On the other hand both stepwise formation constants for zinc(II) and manganese(II) chelates of the sulfonic acid are smaller than the corresponding constants of the 4-hydroxybenzothiazole chelates.

TABLE II

CHELATE FORMATION CONSTANTS OF SUBSTITUTED 4-HYDROXYBENZOTHIAZOLES AT 25° IN 50% V./V. DIOXANE–WATER

	2-Amino-4-hydroxybenzothiazole		4-Hydroxybenzothiazole-7-sulfonic acid	
	log K_1	log K_2	log K_1	log K_2
Cu(II)	11.4	10.5	9.5	7.8
Ni(II)	8.1	7.2	8.1	5.9
Co(II)	7.8	6.8	7.9	5.8
Zn(II)	8.0	7.4	6.1	4.3
Mn(II)	6.2	5.2	5.1	3.9

The formation constants for the divalent metal chelates of 5,7-dibromo-4-hydroxybenzothiazole could not be determined, because of the extreme insolubility of these chelates in 50% v./v. dioxane–water. Approximate values could, however, be calculated for log K_1 in a few instances; log K_1 for copper(II) was 7.1, log K_1 for nickel(II) was 5.4, and log K_1 for cobalt(II) was somewhat lower. The stability order Cu > Ni > Co follows the usual sequence for divalent metals. The lowering of the stability of these metal chelates can be attributed to the decrease in basicity of the nitrogen atom in this ligand.

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