Pure & Appl. Chem., Vol. 69, No. 2, pp. 329–381, 1997.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON EQUILIBRIUM DATA*

Critical Evaluation of

STABILITY CONSTANTS FOR *alpha*-HYDROXYCARBOXYLIC ACID COMPLEXES WITH PROTONS AND METAL IONS AND THE ACCOMPANYING ENTHALPY CHANGES**— PART I: AROMATIC *ortho*-HYDROXYCARBOXYLIC ACIDS

(Technical Report)

Prepared for publication by

LAURI H. J. LAJUNEN[1], ROBERTO PORTANOVA[2], JUHA PIISPANEN[1]
AND MARILENA TOLAZZI[2]

[1]Department of Chemistry, University of Oulu, SF-90570 Oulu, Finland
[2]Department of Chemistry, University of Udine, I-33100 Udine, Italy

*Membership of the Commission in the period (1987–94) during which this Report was prepared was as follows:

Chairman: 1987–89 L. D. Pettit (UK); 1989–92 D. G. Tuck (Canada); 1992–94 T. Kiss (Hungary); *Secretary:* 1987–89 O. Yamauchi (Japan); 1989–92 T. Kiss (Hungary); 1992–94 K. Powell (New Zealand); *Titular Members:* A. C. M. Bourg (1989–91; France); A. Braibanti (1987–93; Italy); R. H. Byrne (1991–95; USA); L. H. J. Lajunen (1991–95; Finland); H. K. J. Powell (1989–95; New Zealand); S. Sjöberg (1993–95; Sweden); D. G. Tuck (1987–95; Canada); P. Valenta (1987–89; FRG); O. Yamauchi (1990–91; Japan); *Associate Members:* A. C. M. Bourg (1987–89; France); R. H. Byrne (1989–91; USA); I. R. Grenthe (1987–89; Sweden); B. Holmberg (1987–91; Sweden); S. Ishiguro (1989–95; Japan); T. A. Kaden (1987–95; Switzerland); T. Kiss (1987–89; Hungary); S. H. Laurie (1989–95; UK); P. A. Manorik (1987–91; USSR); R. P. Martin (1987–93; USA); P. Paoletti (1987–93; Italy); R. Portanova (1987–95; Italy); H. J. K. Powell (1987–89; New Zealand); S. Sjöberg (1989–91; Sweden); O. Yamauchi (1991–95; Japan); *National Representatives:* C. B. Melios (1991–95; Brazil); M. P. Zhang (1989–95; Chinese Chemical Society); P. Valenta (1989–93; FRG); L. H. J. Lajunen (1987–91; Finland); M. T. Beck (1987–91; Hungary); P. K. Bhattacharya (1987–95; India); M. C. Vaz (1991–95; Portugal); H. Ohtaki (1987–91; Japan); C. Luca (1987–89; Romania); S. Ahrland (1987–91; Sweden); I. Tor (1989–91; Turkey); L. D. Pettit (1989–91; UK); G. R. Choppin (1987–89; USA); K. I. Popov (1989–95; Russia).

**Series Title: Critical Evaluation of Stability Constants of Metal Complexes in Solution

Critical evaluation of stability constants for *alpha*-hydroxycarboxylic acid complexes with protons and metal ions and the accompanying enthalpy changes—Part I: Aromatic *ortho*-hydroxycarboxylic acids

Abstract:
Stability constants for different aromatic *ortho*-hydroxycarboxylic acid complexes in aqueous solutions with protons and metal ions published between 1970 and the end of 1993 have been critically evaluated.

1. INTRODUCTION

Hydroxycarboxylic acids form a large group of compounds which are important in many branches of science and technology. Various hydroxycarboxylic acids are also found commonly in nature. They are capable of forming stable metal complexes both in aqueous and nonaqueous solution. Due to the large number of data published in the literature dealing with hydroxycarboxylic acids, in this paper we only review those stability constants for different *ortho*-hydroxycarboxylic acid complexes in aqueous solutions with protons and metal ions published between 1970 and the end of 1993. For comparison, some data published earlier than 1970 are included. In some cases, data obtained in aqueous solutions are compared to those obtained in solvent mixtures like water-ethanol or water-DMSO. In addition to the stability constants, the enthalpy changes of those systems which are available are included. There are a number of papers in the literature concerning the mixed ligand complex formation involving hydroxycarboxylic acids, but these data are not evaluated in this review.

ortho-Hydroxycarboxylic acids form complex compounds with a number of metal ions. The stability constants for complex formation are important, for instance, in understanding how a drug substance operates in body fluids, in modelling natural waters, or in developing new analytical methods and technological processes. Humus substances which normally originate from lignin degradation contain large amounts of aromatic subunits, which are potential ligands for metal ions. These subunits include groups in which one phenolic and one carboxylic group are in an *ortho*-position to each other (salicylic acid). Citric and tartaric acids are very common in various plants; for example, plants absorb trace metals by their roots as citrato complexes. Salicylates are used as food

preservatives. In addition, salicylic acid and its derivatives have been widely used in medicine (aspirin) and analytical chemistry. One of the best known spectrophotometric method for the determination of iron is based on the complex formation between iron(III) and 5-sulfosalicylic acid.

1.1. Presentation of Equilibrium Data

In this evaluation, protonation constants and stability constants are used for proton and metal complexes, respectively.

The protonation constants of *ortho*-hydroxycarboxylic acids are expressed as stepwise protonation constants. For example, in the case of salicylic acid for the equilibria

$$H^+ + L^{2-} = HL^- \text{ (protonation of phenolate group)} \quad (1)$$

$$H^+ + HL^- = H_2L \text{ (protonation of carboxylate group)} \quad (2)$$

the constant K_1 relates to the first of these equilibria, and K_2 to the second:

$$K_1 = [HL^-]/[H^+][L^{2-}] \quad (3)$$

$$K_2 = [H_2L]/[H^+][HL^-] \quad (4)$$

The formation constants of metal complexes may be expressed either by the overall stability constants β_1, β_2, ..., β_n, or by the stepwise stability constants K_1, K_2, ..., K_n as follows (charges are omitted):

$$K_n = [ML_n]/[ML_{n-1}][L] \quad (5)$$

$$\beta_n = [ML_n]/[M][L]^n \quad (6)$$

In this review the stepwise stability constants are used for the formation of ML_n complexes. For the formation of protonated, hydroxo, or polynuclear complex species, the overall stability constants are used:

$$\beta(M_pH_qL_r) = [M_pH_qL_r]/[M]^p[H]^q[L]^r \quad (7)$$

Negative q-values for [H] refer to the formation of mixed hydroxo complexes or equilibria in which one or more hydrogen ions which do not normally dissociate are liberated.

In the Tables the notations L^{2-}, HL^- and H_2L refer to the reactions $M^{m+} + L^{n-} \leftrightarrow ML^{m+n}$, $M^{m+} + HL^{(n-1)-} \leftrightarrow ML^{m+n} + H^+$ and $M^{m+} + H_nL \leftrightarrow ML^{m+n} + nH^+$, respectively.

1.2. Data Evaluation Criteria

The data published in the literature between 1970 and 1993 have been surveyed by considering the following general criteria (91K):

(1) The degree of specification of the experimental conditions (*viz.* the purity of the reagents, temperature, ionic medium, ionic strength, *etc.*).

(2) The calibration of the apparatus used (especially, the calibration of the electrode system in potentiometric measurements).

(3) Definition of the equilibrium constants reported.

(4) The pH and concentration ranges over which the measurements have been carried out, the number of experiments, and the titrant used.

(5) Details of the calibration methods employed, and reliable treatment of the experimental data including statistical analysis of the data and the values of nonvariable constants used (*i.e.* ionization product of water, hydrolysis constants, *etc.*)

(6) Supporting methods.

On the basis of these criteria, data were evaluated and grouped in four categories: recommended (R), tentative (T), doubtful (D), and rejected (Rj), according to the guidelines published earlier (75CE). In addition the data for protonation equilibrium which passed the acceptance criteria were then averaged (providing that enough constants were available), and depending on the values of standard deviation (σ), the average values [$\lg(K \pm \sigma)$] were regarded as recommended ($\sigma < 0.05$), or tentative ($0.05 < \sigma < 0.3$). If stability constants for a particular metal - ligand system have been determined only from one datum, the values are regarded as tentative.

2. GENERAL REMARKS

2.1. Protonation

The compounds reviewed possess one hydroxyl and one carboxyl group *ortho* to each other in an aromatic ring. In addition to these two functional groups, other ionizable or non-ionizable groups may also be present in these compounds.

Due to intramolecular hydrogen bonding between the neighbouring OH- and COOH-groups, and the basic nature of the OH-group, the protonation of the phenolate group takes place at a very high pH level. Because of this *ortho*-effect the protonation constant of the phenolate group of various aromatic *ortho*-hydroxycarboxylic acids is significantly higher than that of phenol [$\lg(K_1/M^{-1}) = 9.79$ at $I_c = 0.5$ M and 25 °C (68M), where I_c denotes the ionic strength and M = mol dm^{-3}], and the protonation constant of the carboxylate group is significantly smaller than that of benzoic acid (77MS). For instance, in 3,5-dihydroxybenzoic acid, there is no intramolecular hydrogen bonding, and the values of the protonation constants of the hydroxylate groups and the carboxylate group are much closer to those for phenol and benzoic acid, respectively (80LS). In addition to the *ortho*-effect,

there are of course, the inductive effect, the mesomeric effect and the charge effect of the different functional groups which affect the dissociation of the "acidic" protons. The positive mesomeric effect of the hydroxyl group is especially worth noting.

As a consequence of intermolecular hydrogen bonding, hydroxycarboxylic acids tend to dimerize in the pure form and in many non-polar solvents. In the solid state and in organic solvents, salicylic acid has been found to exist as the cyclic dimer, H_4L_2, the association taking place through the intermolecular hydrogen bonds formed by the carboxyl groups (51C). As the intramolecular hydrogen bonding is so strong in salicylic acid, Lee (76Ld) has suggested that these bonds persist in the dimers H_4L_2 and $H_3L_2^-$. Lee has further assumed that in solution the neutral dimer of salicylic acid, H_4L_2, would exist in a form similar to that of $H_3L_2^-$ and probably not in the cyclic form occuring in the solid state. According to their assumption, the structure of $H_3L_2^-$ is an open dimer where the association takes place through one hydrogen bond between the carboxyl groups. Similar dimerization has also been observed in aqueous solutions of various dihydroxybenzoic acids, and of 3-bromo-5-sulfosalicylic acid (76Ld and 80LS). According to these studies, these acids dimerize in aqueous solution, but only slightly and only in concentrated solutions. The dimerization is diminished by the intramolecular hydrogen bonds. It is also evident that the dimerization also depends on the acid strength of the carboxyl group. For example, the maximum fractions of the dimers are about 20, 12 and 0.3 % for 3,5-dihydroxybenzoic acid at total concentrations of 0.1, 0.05 and 0.01 M, respectively, while the corresponding values for 2,4-dihydroxybenzoic acid are 4.5, 2.2 and 0.2 % at total concentrations of 0.032, 0.016 and 0.008 M, respectively (80LS).

Due to the very weak dissociation of the hydroxyl group of various aromatic *o*-hydroxycarboxylic acids in aqueous solutions, the corresponding protonation constants determined potentiometrically by using a glass electrode differ from each other, and from those determined by other methods. Those values which are obtained either by spectrophotometric methods or by using a hydrogen electrode for determination of pH can be regarded as more reliable.

Due to the formation of intramolecular hydrogen bonds between phenolate and carboxylate groups, the protonation heat of the phenolate group of salicylic-type ligands differs significantly from that of various benzoate ligands.

2.2. Metal Complex Formation

Salicylic acid and *o*-hydroxynaphthoic acid, as well as their derivatives, can form three types of metal complexes, *viz.* $M(HL)_i$, ML_i, and $M_p(OH)_qL_i$, depending on the pH of the solution. In the acidic region, these acids may form $M(HL)_i$-complexes, in which the hydroxyl group is not deprotonated. In less acidic regions ML_i-chelates can be expected to form in which the coordination takes place via the oxygen atoms of the phenolate and carboxylate groups. In basic solutions various soluble hydroxo species, $M_p(OH)_qL_i$ have been reported to form with some metal ions, like aluminium(III) and lanthanide(III) ions.

Transition metal ions and some ions of the main group elements, like Fe^{3+}, Cu^{2+}, Be^{2+} and Al^{3+}, tend to form relatively stable metal complexes with various aromatic o-hydroxycarboxylic acids. In many case, the formation of the ML complex takes place at such an acidic pH region that it is not possible to determine the stability of this complex by conventional potentiometric titrations, and for example, spectrophotometric methods are used to evaluate the corresponding constants.

Iron(III) forms much more stable complexes with these ligands than does iron(II). In addition these iron(III) complexes are strongly coloured, and they can be used, for instance, for the spectrophotometric determination of iron at the mg/kg level. The determination of iron by means of 5-sulfosalicylic acid is well known, but an even more sensitive and selective determination can be performed with 1-hydroxy-4-sulfo-2-naphthoic acid (79LP). These acids can also be used for the separation of iron from other metal cations connected to ion exchange techniques.

Aluminium(III) forms together with mononuclear AlL_i (i = 1 and 2) complexes a great variety of mononuclear and polynuclear hydroxy species with salicylic acid and its derivatives (83ÖS).

Protonated, $M(HL)_i$, and mononuclear, ML_i, complexes, as well as soluble hydroxo species, $M_p(OH)_qL_i$, have been reported to form in aqueous solutions in lanthanide(III) - *o*-hydroxycarboxylic acid systems. Most of the papers deal with the complex formation of the M(HL)-complexes (H denotes the proton of the hydroxyl group next to the carboxylate group). For example, in the pH range from 3 to 9, the following complex species have been found to form in the lanthanide(III) - 3-bromo-5-sulfosalicylic acid system: $LnHL^+$, LnL, LnL_2^{3-}, $Ln(OH)L^-$, and $Ln(OH)_2L^{2-}$ (93AL).

The stability of the 1:1 lanthanide(III) complexes (LnL) with alkyl and aryl monocarboxylate anions show a good linear correlation with the ligand basicity as measured by the pK_a values of the parent acids (82CB). The corresponding stability constants of lanthanide(III) complexes with many sulfo-substituted aromatic *o*-hydroxycarboxylic acids also show a linear correlation with pK_a, but are more than an order of magnitude greater than those for the lanthanide(III) monocarboxylates. The stabilities of the 3,5-dihydroxybenzoato complexes fall on the common line of alkyl and aryl monocarboxylato complexes, but the values for 2,4- and 2,5-dihydroxybenzoates lie between this line and that for various aromatic sulfo-substituted *o*-hydroxycarboxylato ligands (93AK, 93AL). The higher stability involving the *o*-hydroxycarboxylates were attributed to chelate formation involving the carboxylate and hydroxyl oxygens (86CL, 90RP, 77BB). However, the ^{13}C NMR spectroscopic data might also be interpreted to show the absence of chelate formation in these protonated complexes (93AK, 93AL), and the higher stability of the salicylato complexes has been explained by the mesomeric effect of the hydroxyl group *ortho* to the carboxylic acid group. It has also been suggested that sulfonic acid groups can stabilize the complex by an outer-sphere electrostatic attraction (84NH). The stability constants of LnL complexes in which the hydroxyl group is also deprotonated are much larger than the corresponding stability constants of the Ln(HL) complexes, which is a clear indication of the chelate structure in LnL. The variation of $\log \beta_{101}$ ($\lg K_1$) values as a function of the lanthanide atomic numbers shows a tetrad effect (71FS, 86LL, 93AL), whereas $\lg \beta_{1(11)}$ shows no such a correlation.

3. EVALUATION OF STABILITY CONSTANTS OF COMPLEXES WITH AROMATIC *ortho*-HYDROXYCARBOXYLIC ACIDS

3.1. 2-Hydroxybenzoic Acid (Salicylic Acid), $C_7H_6O_3$

3.1.1. Protonation

Salicylic acid (H_2L) has two ionizable hydrogen ions, which are the protons of the hydroxyl and carboxyl groups. K_1 and K_2 are the corresponding protonation constants of the phenolate and carboxylate groups, respectively (Table 1). Due to reasons explained above, the deprotonation of the hydroxyl group takes place at a very high pH value, which makes the use of a glass electrode unreliable in determining the corresponding protonation constant. Most of the determinations have been carried out in aqueous solutions at relatively low ionic strengths (< 0.2 M) potentiometrically using a glass electrode, but measurements have been also performed spectrophotometrically. In this case, the spectrophometric method should be regarded as the more reliable. In water-ethanol mixtures, the values of the constants are considerably larger than those obtained in aqueous solution. The $\lg(K_2/M^{-1})$ values increase from about 3 to 4 with increasing DMSO concentration from 0 to 45%. Also constants measured in DMSO and dioxane are higher than those in aqueous solutions (77AR). Several values reported in the literature have been rejected because of inadequate experimental data. The average values of the accepted constants (R and T) in 0.1 - 0.2 M solutions at 25 °C are $\lg(K_1/M^{-1}) = 13.44 \pm 0.26$ (T) and $\lg(K_2/M^{-1}) = 2.78 \pm 0.07$ (T).

Protonation enthalpy values are collected in Table 2.

TABLE 1. Protonation Constants of Salicylic Acid $C_7H_6O_3$ [gl = glass electrode (potentiometry), sp = spectrophotometry, cal = calorimetry, con = conductometry]

Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
gl	30	0.05 ($NaClO_4$)	13.25	3.20	85AS	D
gl	30	0.1 (KNO_3)	13.60	2.99	79SV	T
gl	25	0.1 (KNO_3)		2.83	84CT	R
gl	25	1.0 (KNO_3)		2.82	84CT	T
gl	35	0.1 (KNO_3)	12.87	2.75	85KS	T
gl	35	0.1 (KNO_3)		3.11	77JK	D
gl	35	0.1 ($NaClO_4$)	13.24	2.52	76ABa	D
gl	25	0.1 ($NaClO_4$)	13.0	2.82	87GM	T
gl	25	0.4 ($NaClO_4$)	13.0	2.73	87GM	T
gl	25	0.7 ($NaClO_4$)	13.0	2.84	87GM	T
gl	10	0.25		2.78	85DD	T
gl	25	0.25		2.74	85DD	T
gl	37	0.25		2.73	85DD	T

cont'd

TABLE 1. Protonation Constants of Salicylic Acid $C_7H_6O_3$ (continued)

gl	45	0.25		2.73	85DD	T
gl	25	⇒ 0		2.93	85DD	T
gl	25	0.6 (NaCl)		2.724	83ÖS	T
gl	25	1.0 ($NaClO_4$)		2.88	87MM	T
gl	25	0.25 ($NaNO_3$)		2.759	88DO	T
gl	25	0.1 ($NaClO_4$)	13.3	3.1	82DJ	D
gl	25	0.12 (NaCl)	14.0	2.78	81RM	T
gl	37	0.15 ($NaClO_4$)	13.0	2.765	78AK	T
gl	35	0.1 ($NaClO_4$)	13.24	2.82	79A	T
gl	25	0.2 ($NaClO_4$)		2.88	84MA	T
gl	35	0.2 ($NaClO_4$)		2.87	84MA	T
gl	45	0.2 ($NaClO_4$)		2.81	84MA	T
gl	25	0.1 ($NaClO_4$)	12.06	2.82	79LT	D
gl	25	0.1 (KNO_3)	13.60	2.57	84VS	T
sp	25	0.1 (KNO_3)	13.39		84CT	T
sp	25	1.0 (KNO_3)	12.92		84CT	T
sp	25	0.1 ($NaClO_4$)		2.81	81LL	R
sp	25	0.2 ($NaClO_4$)	13.3		82CS	T
sp	25	0.1 ($NaClO_4$)		2.77	82CS	R
sp	25	0.2 ($NaClO_4$)		2.72	82CS	T
sp	25	0.1 ($NaClO_4$)	13.24	2.81	82C	T
sp	25	0.1 ($NaClO_4$)	13.61	2.83	83LE	T
cal	25	?		3.00	77AR	Rj
gl	25	0 (NaCl)		3.008	75LS	T
con	25	0 (NaCl)		2.996	75LS	T
sp	10	0	14.0	2.98	75DI	T
sp	25	0	13.7	3.03	75DI	T
sp	40	0	13.4	3.04	75DI	T
sp	55	0	13.1	3.03	75DI	T
sp	70	0	12.8	3.01	75DI	T
sp	85	0	12.3	2.96	75DI	T
sp	25		13.80	2.97	82GS	Rj
sp	25	0	13.693	2.98	89YA	T
gl	25	0.2	13.4	2.75	90JK	T
gl	25	0.1 ($NaClO_4$)		2.72	89HM	T
gl	25	0.2 (KCl)	13.4	2.79	93KA	T

TABLE 2. Protonation Enthalpies of Salicylic Acid (T = temperature variation)

Method	t/°C	I_c/M	ΔH_1/kJ mol^{-1}	ΔH_2/kJ mol^{-1}	Reference	Category
T	25	0		-3	85DD	D
T	25	0	-33.5	-2.51	82DJ	T
cal	25	?		2.26	77AR	Rj

3.1.2. Stability Constants of the Metal Complexes

Stability constants of metal salicylates are given in Table 3. Several papers deal with 3d-transition metal complexes, like salicylates of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions. Alkali metal ions form very weak complexes with salicylic acid. In the case of alkaline earth metal ions stability constants of the corresponding complexes increase with decreasing ionic radius [$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$]. However, the data published for the Sr^{2+} and Ba^{2+} complexes are inadequate.

The complexation between boric and salicylic acids can be expressed by the following equilibrium:

$$B(OH)_3 + HL^- = LB(OH)_2^- + H_2O \qquad (8)$$

Values obtained spetrophotometrically or potentiometrically by different authors are in agreement with each other (77Q, 78MB, 79QD, 88LTb).

For the main group elements, Al^{3+} forms relatively stable complex compounds with salicylic acid. In addition to two mononuclear AlL^+ and AlL_2^- -complexes, two water-soluble $Al(OH)L_2^{2-}$ and $Al(OH)_2L_2^{3-}$ -hydroxocomplexes are formed and the corresponding formation constants have been determined potentiometrically. ^{27}Al NMR spectroscopic data support this model of four complex compounds together with a set of hydrolysed Al^{3+} species (83ÖS).

The stabilities of the salicylato complexes of bivalent 3d-transition metal ions obey the Irving-Williams stability order. The stability of Fe^{3+} salicylates are considerably higher than those of Fe^{2+} (82C). Complexation of Ln^{3+} ions with salicylic acid should be studied more throughly, and the values available can be regarded as tentative.

Enthalpy changes in formation of metal salicylates are given in Table 4.

TABLE 3. Stability Constants of Salicylic Acid Complexes $C_7H_6O_3$ [M = metal electrode (potentiometry), ix = ion exchange, elph = electrophoresis, dis = distribution between two phases, pol = polarography]

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
Na^+	gl	25	0.25	-0.5			85DD	D
	gl	25	⇒0	-0.31			85DD	D
K^+	gl	25	0.25	-0.5			85DD	D
	gl	25	⇒0	-0.31			85DD	D
Be^{2+}	gl	35	0.1 (KNO_3)	13.12	8.9		77JK	T
	gl	35	0.1 ($NaClO_4$)	12.69	9.65		84A	T
	gl	25	0.1 ($NaClO_4$)	11.45	8.84		79LT	T

cont'd

TABLE 3. Stability Constants of Salicylic Acid Complexes $C_7H_6O_3$ (continued)

Mg^{2+}	gl	37	0.15 ($NaClO_4$)	5.156	78AK	T
	sp	25	0.5 (NaCl)	-8.48 (HL^-)	90DO	T
	M	25	0.03 (NaCl)	1.35	82EF	D
Ca^{2+}	gl	10	0.25	0.53	85DD	D
	gl	25	0.25	0.63	85DD	D
	gl	37	0.25	0.74	85DD	D
	gl	45	0.25	0.80	85DD	D
	gl	25	⇒0	0.72	85DD	D
	gl	37	0.15 ($NaClO_4$)	4.290	78AK	T
	sp	25	0.5 (NaCl)	β_{111} -0.58 (HL^-)	90DO	T
	sp	25	0.5 (NaCl)	-10.19 (HL^-)	90DO	T
B^{3+}	sp	25	0.1 ($NaClO_4$)	1.04 (HL^-)	88LTb	R
	sp	5	0.1 (NaCl)	1.37 (HL^-)	79QD	T
	sp	15	0.1 (NaCl)	1.19 (HL^-)	79QD	T
	sp	25	0.1 (NaCl)	1.04 (HL^-)	79QD	R
	sp	25	0.1 (NaCl)	1.03 (HL^-)	77Q	R
	gl	20	0.1 (KNO_3)	1.23 (HL^-)	78MB	T
	sp	25	0.1	K(M + HL = MHL)7.131	85PM	D
Al^{3+}	gl	25	0.12 (NaCl)	13.7 13.1 10.7	81RM	T
	gl	25	0.6 (NaCl)	β_{101} -3.052 (H_2L)	83ÖS	T
	gl	25	0.6 (NaCl)	β_{102} -8.391 (H_2L)	83ÖS	T
	gl	25	0.6 (NaCl)	β_{1-12} -15.99 (H_2L)	83ÖS	T
	gl	25	0.6 (NaCl)	β_{1-22} -25.31 (H_2L)	83ÖS	T
	gl	25	0.2 (KCl)	13.22 10.51	93KA	T
	gl	25	0.2 (KCl)	β_{2-22} 17.9	93KA	T
	gl	25	0.2 (KCl)	β_{1-12} 16.60	93KA	T
Ga^{3+}	sp	25	0.2 ($NaClO_4$)	0.73 (HL^-)	82CS	R
	gl	25	0.2 ($NaClO_4$)	0.69 (HL^-)	82CS	R
	gl	25	0.2 ($NaClO_4$)	3.16 3.00	84MA	D
	gl	35	0.2 ($NaClO_4$)	3.20 3.04	84MA	D
	gl	45	0.2 ($NaClO_4$)	3.27 3.08	84MA	D
	sp	25	0.1 ($NaClO_4$)	1.19 (HL^-)	77PS	T
	gl	20	0.1 ($NaClO_4$)	16.10	85SA	D
In^{3+}	gl	20	0.1 ($NaClO_4$)	14.28	85SA	D
VO^{2+}	gl	30	0.1 (KNO_3)	13.18	79SV	T
	gl	25	0.1 ($NaClO_4$)	12.683	87GM	T
	gl	25	0.4 ($NaClO_4$)	12.518	87GM	T
	gl	25	0.7 ($NaClO_4$)	12.562	87GM	T
	gl	25	0.2	12.97 9.84	90JK	T
	gl	25	0.2	β_{1-12} 13.16	90JK	T
	gl	25	0.2	β_{1-11} 6.32	90JK	T
	gl	25	0.2	β_{2-22} 16.61	90JK	T
Cr^{3+}	sp	22	0.5 ($NaClO_4$)	K(M + HL = MHL)3.47	77FB	D
	sp	22	0.5 ($NaClO_4$)	K(M + 2HL = $M(HL)_2$) 6.24	77FB	D
	sp	22	0.5 ($NaClO_4$)	K(M + 3HL = $M(HL)_3$)8.41	77FB	D
Mn^{2+}	gl	35	0.1 (KNO_3)	6.10	85KS	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	16.19	82C	T
	sp	25	0.1 ($NaClO_4$)	16.45	83LE	T

cont'd

TABLE 3. Stability Constants of Salicylic Acid Complexes $C_7H_6O_3$ (continued)

	gl	25	0.1 ($NaClO_4$)		12.67	11.77	83LE	T
	sp	25	0.3	16.3	15.4	7.8	86PS	D
	sp	24	0.2 ($NaClO_4$)	15.79	7.68		79DD	T
Co^{2+}	gl	35	0.1 (KNO_3)	6.83			85KS	T
	sp	25		8.09			82GS	Rj
	ix	?		0.90 ?			80CK	Rj
	gl	25	0.1 ($NaClO_4$)	6.15			80MS	T
Ni^{2+}	gl	35	0.1 (KNO_3)	6.80			85KS	T
	gl	35	0.1 ($NaClO_4$)	6.96	4.82		76ABa	T
	sp	25		8.17			82GS	Rj
	ix	?		0.91 ?			80CK	Rj
	sp	25	0.154 ($NaClO_4$)	14.32 (L^{2-})			80YA	D
	sp	25	0.154 ($NaClO_4$)	0.63 (HL^-)			80YA	D
	sp	25	0.154 ($NaClO_4$)	-2.35 (H_2L)			80YA	D
	elph	40	0.1 ($NaClO_4$)	3.0			81SY	D
	gl	30	0.5 (KNO_3)	6.73	7.00		81EE	T
Cu^{2+}	gl	30	0.05 ($NaClO_4$)	9.97	7.66		85AS	T
	gl	25	0.1 (KNO_3)	10.63	8.36		84CT	T
	gl	25	1.0 (KNO_3)	9.81	7.75		84CT	R
	M	25	1.0 (KNO_3)	9.74	7.79		84CT	R
	gl	35	0.1 (KNO_3)	9.84			85KS	T
	gl	35	0.1 ($NaClO_4$)	10.31	7.98		76ABa	T
	gl	25	0.1 ($NaClO_4$)	10.884	9.43		83LL	R
	ix	25	0.01 (KNO_3)	6.6			79VK	D
	gl	25	0.1 ($NaClO_4$)	10.7	7.8		82DJ	T
	gl	37	0.15 ($NaClO_4$)	10.045	6.975		78AK	T
	sp	25		10.67			82GS	Rj
	gl	35	0.1 ($NaClO_4$)	10.45	8.02		79A	T
	elph	40	0.1 ($NaClO_4$)	11.7			81SY	D
	gl	25	0.1 (KNO_3)	10.83	8.05		84VS	R
	gl	30	0.5 (KNO_3)	10.52	8.66		81EE	T
	M	25	0.25 ($NaNO_3$)	-3.00 (HL^-)			88DO	T
	M	25	0.25 ($NaNO_3$)	β_{102} -8.40 (HL^-)			88DO	T
	M	25	0.1 (KNO_3)	10.85			86DV	R
Zn^{2+}	gl	35	0.1 (KNO_3)	7.10			85KS	T
	dis	30	0.1 ($NaClO_4$)	K(M + HL = MHL)1.4			83B	T
	gl	30	0.5 (KNO_3)	7.83			81EE	T
Cd^{2+}	ix	?		0.41 ?			80CK	Rj
	dis	30	0.1 ($NaClO_4$)	K(M + HL = MHL)1.9			83B	T
Sc^{3+}	gl	20	0.1 ($NaClO_4$)	14.20			85SA	D
La^{3+}	gl	25	0.2 ($NaClO_4$)	7.35			86LS	T
	gl	25	0.1 (KNO_3)	9.64			86NS	T
	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.80			89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = $M(HL)_2$)3.55			89HM	T
Ce^{3+}	pol	26	1.0 (KCl)	3.47	3.51		81CPa	D
	gl	25	0.2 ($NaClO_4$)	7.55			86LS	T
Pr^{3+}	gl	25	0.2 ($NaClO_4$)	7.73			86LS	T
	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.88			89HM	T

cont'd

TABLE 3. Stability Constants of Salicylic Acid Complexes $C_7H_6O_3$ (continued)

	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.70	89HM	T
Nd^{3+}	pol	26	1.0 (KCl)	β_{102} 7.70	81CPb	D
	gl	25	0.2 ($NaClO_4$)	7.83	86LS	T
	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.90	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.56	89HM	T
Sm^{3+}	gl	25	0.2 ($NaClO_4$)	7.99	86LS	T
	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)2.06	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.82	89HM	T
Eu^{3+}	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)2.02	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.90	89HM	T
Gd^{3+}	gl	25	0.1 (KNO_3)	9.98	86NS	T
	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.89	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.78	89HM	T
Tb^{3+}	gl	25	0.1 (KNO_3)	10.11	86NS	T
	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.95	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.86	89HM	T
Dy^{3+}	gl	25	0.1 (KNO_3)	10.26	86NS	T
	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.71	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.76	89HM	T
Ho^{3+}	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.83	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.79	89HM	T
Er^{3+}	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.78	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.59	89HM	T
Tm^{3+}	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.75	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.67	89HM	T
Yb^{3+}	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.78	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.45	89HM	T
Lu^{3+}	gl	25	0.1 ($NaClO_4$)	K(M + HL = MHL)1.65	89HM	T
	gl	25	0.1 ($NaClO_4$)	K(M + 2HL = M(HL)$_2$)3.75	89HM	T
Th^{4+}	gl	20	0.1 ($NaClO_4$)	15.45	85SA	D
UO_2^{2+}	gl	25	0.1 ($NaClO_4$)	12.041 10.029	87GM	T
	gl	25	0.4 ($NaClO_4$)	11.969	87GM	T
	gl	25	0.7 ($NaClO_4$)	12.004	87GM	T
	sp	25	0	13.12 (L^{2-})	89YA	D
	sp	25	0	1.43 (HL^-)	89YA	D
	sp	25	0	-3.55 (H_2L)	89YA	D
	gl	25	0.1 (KNO_3)	11.30	85VS	T
NpO_2^+	sp	25	2.0 ($NaClO_4$)	0.20	90RN	T
	dis	25	1.0 ($NaClO_4$)	0.84	92TI	T

TABLE 4. Formation Enthalpies of Salicylic Acid Complexes

Metal	Method	t/°C	I_c/M	ΔH_1/kJ mol^{-1}	ΔH_2/kJ mol^{-1}	Reference	Category
K^+	T	25	0	8		85DD	D
Ca^{2+}	T	25	0	5		85DD	D
Ga^{3+}	T	35	0.2 ($NaClO_4$)	13.3		84MA	T
Cu^{2+}	T	25	0.1 ($NaClO_4$)	-31.0	-27.2	82DJ	T

3.2. Dihydroxybenzoic Acids (Hydroxysalicylic Acids), $C_7H_6O_4$

3.2.1. Protonation

These ligands are tri-protic acids, H_3L, and the values K_1 and K_2 refer to the protonation constants of the two hydroxylate groups, and K_3 to that of the carboxyl group. The protonation constants of 6-hydroxysalicylic acid deviate most significantly from the 3-, 4- and 5-hydroxysalicylic acids (Tables 5 - 8). The lg K_1 and lg K_2 of 6-hydroxysalicylic acid are about of the same magnitude, whereas the values of other dihydroxybenzoic acids differ by about 2 lg units. The lg K_3 value is also considerably lower for the 6-hydroxy derivative than for other hydroxysalicylic acids. These differences can be explained by the two symmetric intramolecular hydrogen bonds formed between the hydroxyl groups and the carboxyl oxygens. The mesomeric effect of the hydroxyl groups also promotes the dissociation of the carboxylate proton (80LS, 89KKa). The average values of the accepted constants for 3-hydroxysalicylic acid in 0.2 M solution at 25 °C are lg(K_2/M^{-1}) = 9.86 ± 0.04 (R) and lg(K_3/M^{-1}) = 3.00 ± 0.27 (T). For 4-hydroxysalicylic acid and 5-hydroxysalicylic acid these values in 0.1 - 0.2 M solutions are lg(K_2/M^{-1}) = 9.02 ± 0.51 (T), lg(K_3/M^{-1}) = 3.08 ± 0.07 (T) and lg(K_2/M^{-1}) = 10.10 ± 0.07 (T), lg(K_3/M^{-1}) = 2.82 ± 0.11 (T), respectively. The average values for 5-hydroxysalicylic acid in 0.5 M solution are lg(K_1/M^{-1}) = 13.13 ± 0.55 (T), lg(K_2/M^{-1}) = 10.07 ± 0.10 (T) and lg(K_3/M^{-1}) = 2.81 ± 0.11 (T).

TABLE 5. 2,3-Dihydroxybenzoic Acid $C_7H_6O_4$

Metal	Method	t/°C	I_c/M	lg(K_1/M^{-1})	lg(K_2/M^{-1})	lg(K_3/M^{-1})	Reference	Category
H^+	sp	25		10.0	8.60		84HM	Rj
	gl	25	1.0 ($NaClO_4$)	13.0	9.76	2.70	86AD	T
	gl	27	0.02-0.13	13.1	10.06	2.70	78AS	T
	gl	25	0.2 ($NaClO_4$)	>14	9.80	2.66	89KKb	T

cont'd

TABLE 5. 2,3-Dihydroxybenzoic Acid $C_7H_6O_4$ (continued)

	gl	25	0.2 (KNO_3)	12.4	9.9	3.01	82HO	T
	gl	25	0.2 (KCl)	>14	9.87	3.32	93KA	T
Al^{3+}	gl	25	0.2 (KCl)	10.32	7.94		93KA	T
	gl	25	0.2 (KCl)	$\beta_{1\text{-}12}$ 11.56			93KA	T
	gl	25	0.2 (KCl)	$\beta_{1\text{-}22}$ 1.74			93KA	T
	gl	25	0.2 (KCl)	$\beta_{2\text{-}22}$ 13.62			93KA	T
	gl	25	0.2 (KCl)	$\beta_{2\text{-}32}$ 8.87			93KA	T
VO^{2+}	gl	25	0.2 ($NaClO_4$)	9.97	7.28		90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}12}$ 10.46			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}22}$ 2.00			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}11}$ 4.02			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{2\text{-}22}$ 12.86			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}21}$-2.88			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}31}$-14.13			90JK	T
Mn^{2+}	gl	25	1.0 ($NaClO_4$)	-15.2 (H_2L^-)			87GN	T
Fe^{3+}	gl	27	0.02-0.13	20.5	7.3	4.3	78AS	T
	gl	27	0.02-0.13	β_{111} 23.5			78AS	T
	gl	25	1.0 ($NaClO_4$)	$K(MHL + H_2L = M(HL)_2 + H)$-2.2			87GN	T
	gl	25	1.0 ($NaClO_4$)	$K(M(HL)_2 + H_2L = M(HL)_3 + H)$-4.5			87GN	T
	sp	25	1.0 ($NaClO_4$)	6.95 (H_2L^-)			88XJ	T
Cu^{2+}	gl	25	1.0 ($NaClO_4$)	$K(M + H_2L = MHL + H)$-2.33			86AD	T
	gl	25	1.0 ($NaClO_4$)	$K(MHL + H_2L = M(HL)_2 + H)$-3.38			86AD	T
	gl	25	1.0 ($NaClO_4$)	$K(MHL_2 + H = M(HL)_2 + H)$9.57			86AD	T
	gl	25	1.0 ($NaClO_4$)	$K(ML_2 + H = MHL_2)$8.57			86AD	T
	gl	25	0.2 ($NaClO_4$)	β_{111} 11.86			89KKb	T
	gl	25	0.2 ($NaClO_4$)	β_{101} 7.56			89KKb	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}11}$ 1.90			89KKb	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}21}$ 9.09			89KKb	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}22}$-4.80			89KKb	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{2\text{-}12}$ 13.06			89KKb	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{2\text{-}22}$ 6.75			89KKb	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{3\text{-}22}$ 10.15			89KKb	T
	gl	25	0.2 ($NaClO_4$)	K_1 / K_2 8.64			89KKb	T
Cd^{2+}	gl	25	1.0 ($NaClO_4$)	-15.40	-16.10 (H_2L^-)		89AP	T

TABLE 6. 2,4-Dihydroxybenzoic Acid $C_7H_6O_4$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	0.5 ($NaClO_4$)	13.37	8.56	3.12	80LS	T
	gl	25	0.2 ($NaClO_4$)		9.75	2.96	85LSa	T
	gl	30	0.1 ($NaClO_4$)	14.20		3.33	76SJ	T
	gl	25	⇒0	12.45	10.50	4.60	77DC	T
	gl	25	1.0 ($NaClO_4$)	13.03	8.62	3.12	86AD	T

cont'd

TABLE 6. 2,4-Dihydroxybenzoic Acid $C_7H_6O_4$ (continued)

	gl	25	0.2 ($NaClO_4$)	>14	8.68	3.11	89KKa	T
	gl	25	0.2 (KCl)	>14	8.64	3.09	93KA	T
	gl	25	0.1 ($NaClO_4$)			3.16	93AK	T
Be^{2+}	gl	25	0.5 ($NaClO_4$)	β_{102} 19.803			79LKb	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 20.238			79LKb	T
	gl	25	0.5 ($NaClO_4$)	β_{122} 37.933			79LKb	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 29.018			79LKb	T
	gl	30	0.1 (KNO_3)	18.15	14.95		78SDa	D
Al^{3+}	gl	25	0.2 (KCl)	8.71	6.32		93KA	T
	gl	25	0.2 (KCl)	$\beta_{2\text{-}22}$ 9.1			93KA	T
	gl	25	0.2 (KCl)	$\beta_{1\text{-}12}$ 7.21			93KA	T
VO^{2+}	gl	30	0.1 ($NaClO_4$)	13.30			77SJ	D
	gl	25	0.2 ($NaClO_4$)	8.50	5.72		90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}12}$ 5.93			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}11}$ 1.48			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{2\text{-}22}$ 8.60			90JK	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	9.00			75JK	T
Fe^{3+}	sp	25	1.0 ($NaClO_4$)	K(M + H_2L = MHL + H)2.80			87GN	T
	gl	25	1.0 ($NaClO_4$)	K(MHL + H_2L = $M(HL)_2$ + H)-1.5			87GN	T
	gl	25	1.0 ($NaClO_4$)	K($M(HL)_2$ + H_2L = $M(HL)_3$+H)-4.8			87GN	T
	sp	?		7.145	4.145		77MM	Rj
Co^{2+}	gl	30	0.1 ($NaClO_4$)	10.48			75JK	T
Ni^{2+}	gl	30	0.1 ($NaClO_4$)	10.62			75JK	T
Cu^{2+}	gl	25	⇒0	10.35	8.75		77DC	T
	gl	25	1.0 ($NaClO_4$)	K(M + H_2L = MHL + H)-3.07			86AD	T
	gl	25	1.0 ($NaClO_4$)	K(MHL + H_2L = $M(HL)_2$ + H)-5.00			86AD	T
	gl	25	1.0 ($NaClO_4$)	K(MHL_2 + H = $M(HL)_2$)8.93			86AD	T
	gl	25	1.0 ($NaClO_4$)	K(ML_2 + H = MHL_2)9.44			86AD	T
	gl	25	0.1 ($NaClO_4$)	11.0	9.3		82DJ	D
	gl	25	0.2 ($NaClO_4$)	β_{111} 10.31			89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{122} 21.46			89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{101} 5.97			89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{102} 9.80			89KKa	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}12}$ 0.98			89KKa	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}22}$-8.41			89KKa	T
Zn^{2+}	gl	30	0.1 (NaClO4)	10.34			75JK	T
ZrO^{2+}	gl	30	0.1 (KNO_3)	K(M + HL = MHL)16.55			78SDb	T
Mo^{6+}	sp	25	?	3.47			80JC	Rj
La^{3+}	gl	25	0.2 ($NaClO_4$)	6.09			85LSa	T
	gl	25	0.1 ($NaClO_4$)	β_{121} 1.80 (H_2L^-)			93AK	T
Ce^{3+}	gl	25	0.2 ($NaClO_4$)	6.21			85LSa	T
Pr^{3+}	gl	25	0.2 ($NaClO_4$)	6.34			85LSa	T
	gl	25	0.1 ($NaClO_4$)	β_{121} 1.93 (H_2L^-)			93AK	T
Nd^{3+}	gl	25	0.2 ($NaClO_4$)	6.48			85LSa	T
	gl	30	0.1 ($NaClO_4$)	10.91	9.75		76SJ	D
	gl	25	0.1 ($NaClO_4$)	β_{121} 1.99 (H_2L^-)			93AK	T

cont'd

TABLE 6. 2,4-Dihydroxybenzoic Acid $C_7H_6O_4$ (continued)

Sm^{3+}	gl	25	0.2 ($NaClO_4$)	6.58	85LSa	T
	gl	25	0.1 ($NaClO_4$)	β_{121} 2.04 (H_2L^-)	93AK	T
Eu^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 2.03 (H_2L^-)	93AK	T
Gd^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.92 (H_2L^-)	93AK	T
Tb^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.88 (H_2L^-)	93AK	T
Dy^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.82 (H_2L^-)	93AK	T
Ho^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.81 (H_2L^-)	93AK	T
Er^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.74 (H_2L^-)	93AK	T
Tm^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.83 (H_2L^-)	93AK	T
Yb^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.77 (H_2L^-)	93AK	T
Lu^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.81 (H_2L^-)	93AK	T

TABLE 7. 2,5-Dihydroxybenzoic Acid $C_7H_6O_4$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	0.5 ($NaClO_4$)	12.74	10.00	2.73	80LS	T
	gl	25	0.5 ($NaClO_4$)	13.90	10.20	2.97	85CD	T
	gl	25	0.5 ($NaClO_4$)	12.74	9.995	2.731	78LKa	T
	gl	25	0.1 ($NaClO_4$)	13.9	10.2	3.0	82DJ	T
	gl	25	0.2 ($NaClO_4$)	>14	10.05	2.73	89KKa	T
	gl	25	0.2 (KCl)	>14	10.06	2.75	93KA	T
	gl	25	0.1 ($NaClO_4$)			2.79	93AK	T
Be^{2+}	gl	25	0.5 ($NaClO_4$)	β_{111} 21.839			78LKa	T
	gl	25	0.5 ($NaClO_4$)	β_{122} 41.347			78LKa	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 31.409			78LKa	T
	gl	25	0.5 ($NaClO_4$)	β_{102} 20.972			78LKa	T
Al^{3+}	gl	25	0.5 ($NaClO_4$)	$K(M + HL = MHL)$10.4			85CD	T
	gl	25	0.5 ($NaClO_4$)	$K(M + 2HL = M(HL)_2)$18.15			85CD	T
	gl	25	0.2 (KCl)	9.74	7.43		93KA	T
	gl	25	0.2 (KCl)	$\beta_{2\text{-}22}$ 11.5			93KA	T
	gl	25	0.2 (KCl)	$\beta_{1\text{-}12}$ 9.97			93KA	T
VO^{2+}	gl	25	0.2 ($NaClO_4$)	9.61	6.82		90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}12}$ 7.48			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}11}$ 2.49			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{2\text{-}22}$ 10.58			90JK	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	8.46			75JK	T
Co^{2+}	gl	30	0.1 ($NaClO_4$)	8.64			75JK	T
Ni^{2+}	gl	30	0.1 ($NaClO_4$)	9.40			75JK	T
	gl	30	0.1 ($NaClO_4$)	9.40			78JS	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	11.6	11.2		82DJ	T

cont'd

TABLE 7. 2,5-Dihydroxybenzoic Acid $C_7H_6O_4$ (continued)

	gl	30	0.1 ($NaClO_4$)	11.41 8.98	75JK	T
	gl	25	0.2 ($NaClO_4$)	β_{111} 11.52	89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{122} 23.97	89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{101} 7.18	89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{102} 11.65	89KKa	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}12}$ 1.26	89KKa	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}22}$ -9.67	89KKa	T
Zn^{2+}	gl	30	0.1 ($NaClO_4$)	9.34	75JK	T
Mo^{6+}	sp	25	0.1	2.58	76DV	D
La^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.80 (H_2L^-)	93AK	T
Pr^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.92 (H_2L^-)	93AK	T
Nd^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.93 (H_2L^-)	93AK	T
Sm^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 2.07 (H_2L^-)	93AK	T
Eu^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 2.08 (H_2L^-)	93AK	T
Gd^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.93 (H_2L^-)	93AK	T
Tb^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.83 (H_2L^-)	93AK	T
Dy^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.74 (H_2L^-)	93AK	T
Ho^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.83 (H_2L^-)	93AK	T
Er^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.75 (H_2L^-)	93AK	T
Tm^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.78 (H_2L^-)	93AK	T
Yb^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.75 (H_2L^-)	93AK	T
Lu^{3+}	gl	25	0.1 ($NaClO_4$)	β_{121} 1.74 (H_2L^-)	93AK	T

TABLE 8. 2,6-Dihydroxybenzoic Acid $C_7H_6O_4$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	0.5 ($NaClO_4$)	13.28	12.57	1.20	80LS	T
	gl	25	1.0 ($NaClO_4$)	13.00	12.57	0.91	86AD	T
	gl	25	1.0 ($NaClO_4$)			1.0	82MSb	T
	sp	25	0.3 ($NaClO_4$)	13.1	13.1		87DS	T
	gl	25	0.2 ($NaClO_4$)	>14	13.1	1.0	89KKa	T
	gl	25	0.2 (KCl)	>14	13.1	1.0	93KA	T
Be^{2+}	gl	25	0.5 ($NaClO_4$)	β_{111} 25.203			79LKb	T
	gl	25	0.5 ($NaClO_4$)	β_{122} 48.528			79LKb	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 36.765			79LKb	T
	gl	25	0.5 ($NaClO_4$)	β_{201} 25.089			79LKb	T
Al^{3+}	gl	25	0.2 (KCl)	12.79	10.88		93KA	T
	gl	25	0.2 (KCl)	$\beta_{2\text{-}22}$ 17.2			93KA	T
	gl	25	0.2 (KCl)	$\beta_{1\text{-}12}$ 16.46			93KA	T
VO^{2+}	gl	25	0.2 ($NaClO_4$)	12.25	9.73		90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}12}$ 12.04			90JK	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}11}$ 4.96			90JK	T

cont'd

TABLE 8. 2,6-Dihydroxybenzoic Acid $C_7H_6O_4$ (continued)

	gl	25	0.2 ($NaClO_4$)	$\beta_{2\text{-}22}$ 22.92	90JK	T
Fe^{3+}	sp	25	1.0 ($NaClO_4$)	K(M + H_2L = MHL+H)2.18	87GN	T
	gl	25	1.0 ($NaClO_4$)	K(MHL + H_2L = $M(HL)_2$+H)-1.4	87GN	T
	gl	25	1.0 ($NaClO_4$)	K($M(HL)_2$ + H_2L = $M(HL)_3$+H)-4.6	87GN	T
	sp	25	1.0 ($NaClO_4$)	2.35 (HL^-)	82MSb	T
Ni^{2+}	sp	25	0.3 ($NaClO_4$)	7.30	87DS	T
Cu^{2+}	gl	25	1.0 ($NaClO_4$)	K(M + H_2L = MHL+H)-2.97	86AD	T
	gl	25	1.0 ($NaClO_4$)	K(MHL + H_2L = $M(HL)_2$+H)-4.77	86AD	T
	gl	25	1.0 ($NaClO_4$)	K(MHL_2 + H = $M(HL)_2$)11.84	86AD	T
	gl	25	0.2 ($NaClO_4$)	β_{111} 15.20	89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{122} 30.45	89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{101} 10.19	89KKa	T
	gl	25	0.2 ($NaClO_4$)	β_{102} 18.47	89KKa	T
	gl	25	0.2 ($NaClO_4$)	$\beta_{1\text{-}12}$ 6.45	89KKa	T

3.2.2. Metal Complex Formation

The most studied acid of this group of ligands is 4-hydroxysalicylic acid (Tables 5 - 8). Among the alkaline earth metal ions only the Be^{2+} complex formation has been studied. The stability order of various beryllium(II) dihydroxybenzoato complexes is: 6-hydroxysalicylic acid > 5-hydroxysalicylic acid > 4-hydroxysalicylic acid (79LKb). For instance, in the case of 5-hydroxysalicylic acid, the complexation takes place via the neighbouring OH- and COOH-groups, and with increasing pH the proton of the OH group at the carbon C-5 will be dissociated according to the following reaction:

$$BeHL = BeL^- + H^+ \quad (9)$$

$$BeH_2L_2^{2-} = BeHL_2^{3-} + H^+ \quad (10)$$

$$BeHL_2^{3-} = BeL_2^{4-} + H^+ \quad (11)$$

However, the relative amount of the BeL^- species is so small that no good estimate could be determined for it (78LKa). The data available indicate that 6-hydroxysalicylic acid is also able to form binuclear complex compounds with beryllium(II) and oxovanadium(IV) (79LKb, 90JK).

Complex equilibria of Cu^{2+} ions have been studied with all of these ligands. According to Aplicourt *et al.* (86AD) the $CuH_2L_2^{2-}$ complex (H_3L = 3-, 4- or 6-hydroxysalicylic acid) deprotonates in aqueous solutions to form the $CuHL_2^{3-}$ species. In the case of the 3- and 4-hydroxysalicylate systems, CuL_2^{4-} complexes are also formed.

Protonation enthaplies and metal complex formation enthalpies of 2,4- and 2,5-dihydroxybenzoic acids are given in Table 9.

TABLE 9. Protonation Enthalpies and Metal Complex Formation Enthalpies of 2,4-Dihydroxybenzoic Acid (I) and 2,5-Dihydroxybenzoic Acid (II)

Metal	Ligand	Method	t/°C	I_c/M	ΔH_1/kJ mol^{-1}	ΔH_2/kJ mol^{-1}	Reference	Category
H^+	I	T	25	0.1 ($NaClO_4$)	-31.8	-3.3	82DJ	T
	I	cal	25	0.1 ($NaClO_4$)	ΔH_3 -1.77		93AK	T
	II	T	25	0.1 ($NaClO_4$)	-36.0	-4.2	82DJ	T
	II	cal	25	0.1 ($NaClO_4$)	ΔH_3 -1.88		93AK	T
Cu^{2+}	I	T	25	0.1 ($NaClO_4$)	-32.6	-41.0	82DJ	T
	II	T	25	0.1 ($NaClO_4$)	-41.0	-54.0	82DJ	T
La^{3+}	I	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 1.5 (H_2L^-)		93AK	T
	II	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 3.3 (H_2L^-)		93AK	T
Pr^{3+}	II	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 1.7 (H_2L^-)		93AK	T
Nd^{3+}	II	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 1.6 (H_2L^-)		93AK	T
Sm^{3+}	II	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 1.6 (H_2L^-)		93AK	T
Eu^{3+}	I	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 2.5 (H_2L^-)		93AK	T
Gd^{3+}	II	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 2.0 (H_2L^-)		93AK	T
Tb^{3+}	I	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 3.0 (H_2L^-)		93AK	T
Dy^{3+}	II	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 4.1 (H_2L^-)		93AK	T
Ho^{3+}	II	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 2.5 (H_2L^-)		93AK	T
Er^{3+}	II	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 3.1 (H_2L^-)		93AK	T
Tm^{3+}	I	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 3.8 (H_2L^-)		93AK	T
Lu^{3+}	I	cal	25	0.1 ($NaClO_4$)	ΔH_{121} 4.5 (H_2L^-)		93AK	T

3.3. Halo-substituted Salicylic Acids

3.3.1. Fluoro-substituted Salicylic Acids, $C_7H_5FO_3$

There is only one paper available in the literature concerning protonation and complex formation of fluoro-substituted salicylic acids (89YA), and these results should be regarded as doubtful (Table 10).

TABLE 10. 5-Fluoro-2-hydroxybenzoic Acid $C_7H_5FO_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	0	13.703	2.56	89YA	D
UO_2^{2+}	sp	25	0	13.0 (L^{2-})		89YA	D
	sp	25	0	1.29 (HL^-)		89YA	D
	sp	25	0	-3.27 (H_2L)		89YA	D

3.3.2. Chloro-substituted Salicylic Acids, $C_7H_5ClO_3$ and $C_7H_4Cl_2O_3$

Halogen atom substituents are electron-withdrawing, and thus tend to increase the acidity of the protonated functional groups. This can be seen in the pK_a values of the various halogenated salicylic acids in comparison to the corresponding values of salicylic acid. The acidity of the OH-group in salicylic acids increases in the following order: salicylic acid < chlorosalicylic acid < bromosalicylic acid < iodosalicylic acid (83LE). The acidity of the dichloroderivative is even higher than that of monochloro-substituted salicylic acid (82DJ, 83LE). The average values of the accepted protonation constants for 5-chlorosalicylic acid in 0.1 - 0.2 M solution at 25 °C are $\lg(K_1/M^{-1}) = 12.57 \pm 0.24$ (T) and $\lg(K_2/M^{-1}) = 2.45 \pm 0.04$ (R).

TABLE 11. 5-Chloro-2-hydroxybenzoic Acid $C_7H_5ClO_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	30	0.05 ($NaClO_4$)	12.22	2.71		85AS	T
	gl	30	0.1 ($NaClO_4$)	12.50	2.43		76ABb	T
	gl	25	0.1 ($NaClO_4$)	11.87	2.49		79LT	D
	sp	?	?	12.22	2.71		81GS	Rj
	sp	25	0.1 ($NaClO_4$)	12.91	2.48		83LE	T
	sp	?	0.1 (KNO_3)	12.15	2.64		85SB	D
	sp	25	0.2 ($NaClO_4$)	12.4	2.41		82CS	T
	sp	25	0.1 ($NaClO_4$)		2.44		82CS	T
	gl	25	0.2 ($NaClO_4$)		2.42		82CS	T
	sp	25	0	12.947	2.65		89YA	T
	gl	25	0.1 ($NaClO_4$)	12.4	2.51		80MS	T
Be^{2+}	gl	30	0.1 ($NaClO_4$)	11.97	9.30		76ABb	T
	gl	25	0.1 ($NaClO_4$)	11.26	8.78		79LT	T
	gl	25	0.1 ($NaClO_4$)	-3.10 (H_2L)			79LT	T

cont'd

TABLE 11. 5-Chloro-2-hydroxybenzoic Acid $C_7H_5ClO_3$ (continued)

	gl	30	0.1 ($NaClO_4$)	11.05	7.35		83MS	T
	gl	35	0.1 ($NaClO_4$)	10.60	7.20		83MS	T
	gl	40	0.1 ($NaClO_4$)	9.95	7.10		83MS	T
	T	35	0.1 ($NaClO_4$)	ΔH -201.0			83MS	T
B^{3+}	sp	25	0.1 (NaCl)	0.85 (HL^-)			79QD	T
Ga^{3+}	sp	25	0.2 ($NaClO_4$)	0.77 (HL^-)			82CS	T
	sp	25	0.2 ($NaClO_4$)	K(M + HL = MHL)	1.72		82CS	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	6.46			75JK	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	15.25			82C	T
	sp	25	0.1 ($NaClO_4$)	15.74			83LE	T
	gl	25	0.1 ($NaClO_4$)		12.38	10.84	83LE	T
	sp	25	1.0 ($NaClO_4$)	2.80 (HL^-)			82MSb	T
	sp	?	0.1 (KNO_3)	14.96	11.04	8.84	85SB	T
Co^{2+}	sp	25		6.43			83SG	Rj
	gl	30	0.1 ($NaClO_4$)	6.21			75JK	T
Ni^{2+}	sp	25	0.154 ($NaClO_4$)	13.58 (L^{2-})			80YA	D
	sp	25	0.154 ($NaClO_4$)	0.63 (HL^-)			80YA	D
	sp	25	0.154 ($NaClO_4$)	-2.02 (H_2L)			80YA	D
	sp	25		6.49			83SG	Rj
	gl	30	0.1 ($NaClO_4$)	7.82			75JK	T
	gl	25	0.1 ($NaClO_4$)	6.36			80MS	T
Cu^{2+}	gl	30	0.1 ($NaClO_4$)	9.61	7.34		85AS	T
	gl	35	0.1 ($NaClO_4$)	10.05	7.54		81AS	T
	sp	?	?	9.66			81GS	Rj
	gl	25	0.1 ($NaClO_4$)	10.355	8.60		83LL	T
	gl	30	0.1 ($NaClO_4$)	9.67	7.36		75JK	T
Zn^{2+}	gl	30	0.1 ($NaClO_4$)	8.70	6.70		82MSa	T
	gl	35	0.1 ($NaClO_4$)	7.90	6.10		82MSa	T
	gl	40	0.1 ($NaClO_4$)	7.70	5.90		82MSa	T
	T	30	0.1 ($NaClO_4$)	ΔH -182.8			82MSa	T
	gl	30	0.1 ($NaClO_4$)	7.32			75JK	T
UO_2^{2+}	sp	25	0	12.52 (L^{2-})			89YA	D
	sp	25	0	1.58 (HL^-)			89YA	D
	sp	25	0	-3.07 (H_2L)			89YA	D

TABLE 12. 3,5-Dichloro-2-hydroxybenzoic Acid $C_7H_4Cl_2O_3$

Metal	Method	t/°C	I_c/M	lg(K_1/M^{-1})	lg(K_2/M^{-1})	Reference	Category
H^+	gl	25	0.1 ($NaClO_4$)	10.1	2.4	82DJ	T
	gl	30	0.1 ($NaClO_4$)	10.22	2.45	75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -23.0	ΔH_2 -5.0	82DJ	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	4.49		75JK	T
Co^{2+}	gl	30	0.1 ($NaClO_4$)	5.40		75JK	T

cont'd

TABLE 12. 3,5-Dichloro-2-hydroxybenzoic Acid $C_7H_4Cl_2O_3$ (continued)

Ni^{2+}	gl	30	0.1 ($NaClO_4$)	5.98		75JK	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	8.4	5.6	82DJ	T
	gl	30	0.1 ($NaClO_4$)	8.35	5.55	75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -18.0	ΔH_2 -16.7	82DJ	T
Zn^{2+}	gl	30	0.1 ($NaClO_4$)	5.47		75JK	T

3.3.3. Bromo-substituted Salicylic Acids, $C_7H_5BrO_3$ and $C_7H_4Br_2O_3$

The position and number of bromo-substituents have a significant effect on the protonation constants of the various bromo-substituted salicylic acids. The $\lg(K_1/M^{-1})$ values for 3-bromo- and 3,5-dibromosalicylic acids are much smaller than those of 4- and 5-bromosalicylic acids (75JK, 82DJ, 83LE). Bromo-substitution also has an influence on the Cu^{2+} complex formation (83LL) (Tables 13 - 16).

TABLE 13. 3-Bromo-2-hydroxybenzoic Acid $C_7H_5BrO_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	25	0.1 ($NaClO_4$)	10.7	2,7	82DJ	T
	gl	30	0.1 ($NaClO_4$)	10.64	2.83	75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -20.5	ΔH_2 -2.5	82DJ	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	5.33		75JK	T
Co^{2+}	gl	30	0.1 ($NaClO_4$)	5.38		75JK	T
Ni^{2+}	gl	30	0.1 ($NaClO_4$)	6.68		75JK	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	9.2	6.3	82DJ	T
	gl	30	0.1 ($NaClO_4$)	8.70	6.25	75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -20.5	ΔH_2 -18.0	82DJ	T
Zn^{2+}	gl	30	0.1 ($NaClO_4$)	6.42		75JK	T

TABLE 14. 4-Bromo-2-hydroxybenzoic Acid $C_7H_5BrO_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	30	0.1 ($NaClO_4$)	11.70	2.75	75JK	T
Cu^{2+}	gl	30	0.1 ($NaClO_4$)	9.17	7.13	75JK	T

TABLE 15. 5-Bromo-2-hydroxybenzoic Acid $C_7H_5BrO_3$

Metal	Method	t/°C	I_c/M	lg(K_1/M^{-1})	lg(K_2/M^{-1})	lg(K_3/M^{-1})	Reference	Category
H^+	gl	30	0.1 ($NaClO_4$)	12.41	2.40		76ABb	T
	sp	?	?	12.11	2.61		81GS	Rj
	sp	25	0.1 ($NaClO_4$)	12.62	2.48		83LE	T
	sp	25	0	12.850	2.65		89YA	T
Be^{2+}	gl	30	0.1 ($NaClO_4$)	11.84	9.28		76ABb	T
B^{3+}	sp	25	0.1 (NaCl)	0.87 (HL^-)			79QD	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	15.47			83LE	T
	gl	25	0.1 ($NaClO_4$)		12.23	10.64	83LE	T
Co^{2+}	sp	25		6.43			83SG	Rj
Ni^{2+}	sp	25	0.154 ($NaClO_4$)	13.44 (L^{2-})			80YA	D
	sp	25	0.154 ($NaClO_4$)	0.59 (HL^-)			80YA	D
	sp	25	0.154 ($NaClO_4$)	-2.06 (H_2L)			80YA	D
	sp	25		6.48			83SG	Rj
Cu^{2+}	gl	35	0.1 ($NaClO_4$)	10.01	7.45		81AS	T
	sp	?	?	9.37			81GS	Rj
	gl	25	0.1 ($NaClO_4$)	10.186	8.30		83LL	T
UO_2^{2+}	sp	25	0	12.11 (L^{2-})			89YA	D
	sp	25	0	1.26 (HL^-)			89YA	D
	sp	25	0	-3.39 (H_2L)			89YA	D

TABLE 16. 3,5-Dibromo-2-hydroxybenzoic Acid $C_7H_4Br_2O_3$

Metal	Method	t/°C	I_c/M	lg(K_1/M^{-1})	lg(K_2/M^{-1})	Reference	Category
H^+	gl	25	0.1 ($NaClO_4$)	10.5	2.6	82DJ	T
	gl	30	0.05 ($NaClO_4$)	10.43	2.55	85AS	T
	gl	30	0.1 ($NaClO_4$)	10.43	2.55	75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -22.6	ΔH_2 -5.0	82DJ	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	5.03		75JK	T
Co^{2+}	gl	30	0.1 ($NaClO_4$)	5.63		75JK	T
Ni^{2+}	gl	30	0.1 ($NaClO_4$)	6.10		75JK	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	8.4	5.6	82DJ	T
	gl	30	0.05 ($NaClO_4$)	9.30	7.30	85AS	T
	gl	30	0.1 ($NaClO_4$)	8.41	5.60	75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -18.0	ΔH_2 -15.5	82DJ	T
Zn^{2+}	gl	30	0.1 ($NaClO_4$)	6.04		75JK	T

3.3.4. Iodo-substituted Salicylic Acids, $C_7H_5IO_3$, $C_7H_4I_2O_3$

Iodo-substituted salicylic acids are sparingly soluble in water and only one report is available on the protonation and complex formation of 3,5-diiodosalicylic acid (85AS) (Tables 17 and 18).

TABLE 17. 2-Hydroxy-5-iodobenzoic Acid $C_7H_5IO_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	35	0.1 ($NaClO_4$)	12.13	2.38		79A	T
	sp	25	0.1 ($NaClO_4$)	12.36	2.54		83LE	T
	sp	25	0	12.786	2.62		89YA	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	15.35			83LE	T
	gl	25	0.1 ($NaClO_4$)		11.63	9.36	83LE	T
Cu^{2+}	gl	35	0.1 ($NaClO_4$)	9.83	7.41		79A	T
	gl	25	0.1 ($NaClO_4$)	9.845	8.68		83LL	T
UO_2^{2+}	sp	25	0	12.37 (L^{2-})			89YA	D
	sp	25	0	1.59 (HL^-)			89YA	D
	sp	25	0	-3.04 (H_2L)			89YA	D

TABLE 18. 2-Hydroxy-3,5-diiodobenzoic Acid $C_7H_4I_2O_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	30	0.05 ($NaClO_4$)	11.20	3.81	85AS	T
Cu^{2+}	gl	30	0.05 ($NaClO_4$)	8.91	7.19	85AS	T

3.4. Alkyl-substituted Salicylic Acids

3.4.1. Methylsalicylic Acids, $C_8H_8O_3$

The methyl group is a strongly electron-donating group, and thus has an effect opposite to that of halogen-substituents. This is clearly shown by the increased basicity of the OH-group of methylsalicylates. The methyl group diminishes the solubility of salicylic acid in water which causes limitations for the concentration range in experiments in aqueous solutions. There is also evidence that the methyl group in ortho-position (3-methylsalicylic acid) may cause steric hindrance in metal complex formation (76ABb) (Tables 19 - 21).

TABLE 19. 2-Hydroxy-3-methylbenzoic Acid (*o*-Cresotic Acid) $C_8H_8O_3$

Metal	Method	*t*/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	35	0.1 ($NaClO_4$)	14.14	2.84	76ABb	T
	gl	25	⇒0	11.80	4.40	77DC	D
	sp	25	0	15.001	3.00	89YA	T
Be^{2+}	gl	35	0.1 ($NaClO_4$)	13.05	8.78	76ABb	T
VO^{2+}	gl	35	0.1 ($NaClO_4$)	13.00		83IS	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	16.75		82C	T
Cu^{2+}	gl	25	⇒0	9.20	7.75	77DC	D
	gl	35	0.1 ($NaClO_4$)	10.58	6.39	81AS	T
UO_2^{2+}	sp	25	0	14.33 (L^{2-})		89YA	D
	sp	25	0	1.33 (HL^-)		89YA	D
	sp	25	0	-3.67 (H_2L)		89YA	D

TABLE 20. 2-Hydroxy-4-methylbenzoic Acid (*m*-Cresotic Acid) $C_8H_8O_3$

Metal	Method	*t*/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	35	0.1 ($NaClO_4$)	13.54	2.94	76ABb	T
	sp	25	0	14.238	3.19	89YA	T
Be^{2+}	gl	35	0.1 ($NaClO_4$)	12.87	9.89	76ABb	T
VO^{2+}	gl	35	0.1 ($NaClO_4$)	13.40		83IS	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	16.49		82C	T
Ni^{2+}	sp	25	0.154 ($NaClO_4$)	15.46 (L^{2-})		80YA	D
	sp	25	0.154 ($NaClO_4$)	1.22 (HL^-)		80YA	D
	sp	25	0.154 ($NaClO_4$)	-1.97 (H_2L)		80YA	D
Cu^{2+}	gl	35	0.1 ($NaClO_4$)	10.71	8.35	81AS	T
UO_2^{2+}	sp	25	0	13.70 (L^{2-})		89YA	D
	sp	25	0	1.46 (HL^-)		89YA	D
	sp	25	0	-3.72 (H_2L)		89YA	D

TABLE 21. 2-Hydroxy-5-methylbenzoic Acid (*p*-Cresotic Acid) $C_8H_8O_3$

Metal	Method	*t*/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	35	0.1 ($NaClO_4$)	13.74	2.87	76ABb	T
Be^{2+}	gl	35	0.1 ($NaClO_4$)	12.94	9.97	76ABb	T
B^{3+}	sp	25	0.1 (NaCl)	1.05 (HL^-)		79QD	T
VO^{2+}	gl	35	0.1 ($NaClO_4$)	13.49		83IS	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	16.05		82C	T
Cu^{2+}	gl	35	0.1 ($NaClO_4$)	10.83	8.45	81AS	T

3.4.2. Methoxysalicylic Acids, $C_8H_8O_4$

Only one paper is available in the literature on the protonation and complex formation of 3-methoxysalicylic acid. The values reported indicate a minor effect of the 3-methoxy group on protonation and UO_2^{2+} complex formation compared to those of salicylic acid (Tables 22 and 23).

TABLE 22. 2-Hydroxy-3-methoxybenzoic Acid $C_8H_8O_4$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	0	13.948	2.69	89YA	T
UO_2^{2+}	sp	25	0	13.38 (L^{2-})		89YA	D
	sp	25	0	1.43 (HL^-)		89YA	D
	sp	25	0	-3.25 (H_2L)		89YA	D

TABLE 23. 2-Hydroxy-5-methoxybenzoic Acid $C_8H_8O_4$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	0	13.845	2.91	89YA	T
Ni^{2+}	sp	25	0.154 ($NaClO_4$)	14.49 (L^{2-})		80YA	D
	sp	25	0.154 ($NaClO_4$)	0.65 (HL^-)		80YA	D
	sp	25	0.154 ($NaClO_4$)	-2.26 (H_2L)		80YA	D
UO_2^{2+}	sp	25	0	13.15 (L^{2-})		89YA	D
	sp	25	0	1.31 (HL^-)		89YA	D
	sp	25	0	-3.60 (H_2L)		89YA	D

3.5. Nitrosalicylic Acids, $C_7H_5NO_5$, $C_7H_4N_2O_7$ and $C_8H_7NO_5$

The nitro group is a strong electron-withdrawing substituent and has a significant effect, especially, on deprotonation of the OH-group in salicylic acid. The acidity of the OH-group of the mononitrosalicylic acids increases in the following order: salicylic acid < 4-nitrosalicylic acid < 5-nitrosalicylic acid < 3-nitrosalicylic acid. 3,5-Dinitrosalicylic acid is a significantly stronger acid than the three corresponding mononitroderivatives with respect to both the OH- and COOH-groups. The acidity order for the carboxylic acid group is: 3,5-dinitrosalicylic acid > 3-nitrosalicylic acid > 5-nitrosalicylic acid > 6-nitrosalicylic acid > salicylic acid (79LT, 81LL). There are significant differences between some values reported in the literature (82CS, 82MSb).

In nitrosalicylic acids an intramolecular hydrogen bond may be formed either between the COOH- and OH-groups or between the NO_2- and OH-groups. Whether hydrogen bonding exists depends on

the position of the nitro group in the benzene ring. The average values of the accepted protonation constants for 5-nitrosalicylic acid in 0.1 - 0.2 M solutions at 25 °C are $\lg(K_1/M^{-1}) = 9.98 \pm 0.12$ (T) and $\lg(K_2/M^{-1}) = 1.99 \pm 0.14$ (T).

A methyl group in addition to a nitro group in salicylic acid will decrease the acidity of the compound (80NS). Complex equilibria between beryllium(II) and 5-nitrosalicylic acid or 3,5-dinitrosalicylic acid have been studied (76ABb, 79LT). There is a linear relationship between the stability constants of the various borate complexes and the acidity of the ligand acids (88LTb). Aluminium(III) forms very stable nitrosalicylato complexes in aqueous solutions (79LT, 79PT). Protonation and stability constants reported for nitrosalicylic acids are summarized in Tables 24 - 29.

TABLE 24. 2-Hydroxy-3-nitrobenzoic Acid $C_7H_5NO_5$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	?	10.25	1.82	81GS	Rj
	gl	25	0.1 ($NaClO_4$)	10.3	1.8	82DJ	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -18.8	ΔH_2 -5.0	82DJ	T
	sp	25	0.1 ($NaClO_4$)	9.87	1.73	81LL	T
	gl	30	0.1 ($NaClO_4$)	10.22	1.82	75JK	T
B^{3+}	sp	25	0.1 ($NaClO_4$)	0.38 (HL^-)		88LTb	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	4.85		75JK	T
Co^{2+}	sp	25	?	5.76		82GS	Rj
	gl	30	0.1 ($NaClO_4$)	5.24		75JK	T
Ni^{2+}	sp	25	?	5.89		82GS	Rj
	gl	30	0.1 ($NaClO_4$)	5.96		75JK	T
Cu^{2+}	sp	?	?	8.44		81GS	Rj
	gl	25	0.1 ($NaClO_4$)	8.3	5.9	82DJ	T
	gl	30	0.1 ($NaClO_4$)	8.12	5.87	75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -23.0	ΔH_2 -18.0	82DJ	T
Zn^{2+}	gl	30	0.1 ($NaClO_4$)	5.73		75JK	T

TABLE 25. 2-Hydroxy-4-nitrobenzoic Acid $C_7H_5NO_5$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	?	?	10.32	1.43	81GS	Rj
	sp	25	0.1 ($NaClO_4$)	10.91	2.05	81LL	T
B^{3+}	sp	25	0.1 ($NaClO_4$)	0.76 (HL^-)		88LTb	T
Co^{2+}	sp	25	?	5.37		82GS	Rj
Ni^{2+}	sp	25	?	5.46		82GS	Rj
Cu^{2+}	sp	?	?	7.43		81GS	Rj

TABLE 26. 2-Hydroxy-5-nitrobenzoic Acid $C_7H_5NO_5$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	35	0.1 ($NaClO_4$)	9.89	1.90		80A	T
	?	20	0.1	10.63	2.71		80NS	D
	sp	25	0.1		2.24		79PT	T
	gl	35	0.1 ($NaClO_4$)	9.89	1.90		76ABb	T
	gl	25	0.1 ($NaClO_4$)	9.90	1.98		79LT	R
	sp	25	0.1 ($NaClO_4$)	9.89	1.90		82C	R
	sp	25	0.2 ($NaClO_4$)	10.0	1.87		82CS	T
	sp	25	0.1 ($NaClO_4$)		1.91		82CS	T
	gl	25	0.2 ($NaClO_4$)		1.88		82CS	T
	sp	25	0.1 ($NaClO_4$)	9.90	1.96		81LL	R
	sp	25	0	10.343	2.11		89YA	T
	gl	25	0.1 ($NaClO_4$)	10.2	2.2		82DJ	T
	gl	30	0.1 ($NaClO_4$)	10.13	2.22		75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -20.5	ΔH_2 -3.8		82DJ	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	9.64	7.53		79LT	T
	gl	25	0.1 ($NaClO_4$)	-2.24 (H_2L)			79LT	T
	gl	35	0.1 ($NaClO_4$)	9.71	7.86		76ABb	T
B^{3+}	sp	25	0.1 (NaCl)	0.48 (HL^-)			79QD	T
	sp	25	0.1 ($NaClO_4$)	0.69 (HL^-)			88LTb	T
Al^{3+}	sp	25	0.1	1.11 (HL^-)			79PT	T
	sp	25	0.1 ($NaClO_4$)	11.11			79LT	T
	gl	25	0.1 ($NaClO_4$)		8.62	6.13	79LT	T
Ga^{3+}	sp	25	0.2 ($NaClO_4$)	1.40 (HL^-)			82CS	T
	sp	25	0.2 ($NaClO_4$)	K(M + HL = MHL)	1.94		82CS	T
	sp	25	0.1	1.69 (HL^-)			80PS	T
	sp	25	0.1	K(M + HL = MHL)	2.70		80PS	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	4.41			75JK	T
Fe^{3+}	sp	25	1.0 ($NaClO_4$)	3.23 (HL^-)			82MSb	T
	sp	25	0.1 ($NaClO_4$)	12.76			82C	T
Co^{2+}	gl	35	0.1 ($NaClO_4$)	4.98	3.08		83A	T
	gl	30	0.1 ($NaClO_4$)	5.18			75JK	T
Ni^{2+}	sp	25	0.154 ($NaClO_4$)	10.37 (L^{2-})			80YA	D
	sp	25	0.154 ($NaClO_4$)	0.02 (HL^-)			80YA	D
	sp	25	0.154 ($NaClO_4$)	-2.08 (H_2L)			80YA	D
	sp	25	0.3 ($NaNO_3$)	5.62			74HK	T
	gl	30	0.1 ($NaClO_4$)	5.86			75JK	T
Cu^{2+}	?	20	0.1	8.01			80NS	D
	gl	35	0.1 ($NaClO_4$)	8.51	6.11		81AS	T
	gl	25	0.1 ($NaClO_4$)	8.435	6.44		83LL	T
	gl	25	0.1 ($NaClO_4$)	8.0	6.0		82DJ	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -20.1	ΔH_2 -20.5		82DJ	T
	gl	30	0.1 ($NaClO_4$)	7.99	5.94		75JK	T
Zn^{2+}	gl	35	0.1 ($NaClO_4$)	5.12	3.25		80A	T
	gl	30	0.1 ($NaClO_4$)	5.38			75JK	T

cont'd

TABLE 26. 2-Hydroxy-5-nitrobenzoic Acid $C_7H_5NO_5$ (continued)

UO_2^{2+}	sp	25	0	10.53 (L^{2-})	89YA	D
	sp	25	0	2.19 (HL^-)	89YA	D
	sp	25	0	-1.92 (H_2L)	89YA	D

TABLE 27. 2-Hydroxy-6-nitrobenzoic Acid $C_7H_5NO_5$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	0.1 ($NaClO_4$)	9.04	1.99	81LL	T
B^{3+}	sp	25	0.1 ($NaClO_4$)	0.34 (HL^-)		88LTb	T

TABLE 28. 2-Hydroxy-3,5-dinitrobenzoic Acid $C_7H_4N_2O_7$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	sp	?	?	7.01	1.32		81GS	Rj
	gl	25	0.3 ($NaClO_4$)	7.02	0.28		87DS	T
	sp	25	1.0 ($NaClO_4$)		0.49		82MSb	D
	gl	30	0.1 ($NaClO_4$)	7.02	1.31		76SJ	T
	gl	25	0.1 ($NaClO_4$)	7.02	1.34		79LT	T
	gl	30	0.05 ($NaClO_4$)	7.68	1.56		85AS	T
	gl	25	0.2 ($NaClO_4$)	7.05			84MA	T
	gl	35	0.2 ($NaClO_4$)	6.98			84MA	T
	gl	45	0.2 ($NaClO_4$)	6.91			84MA	T
	sp	15	0.2 ($NaClO_4$)		0.27		82CS	D
	sp	25	0.2 ($NaClO_4$)		0.28		82CS	D
	sp	35	0.2 ($NaClO_4$)		0.30		82CS	D
	sp	45	0.2 ($NaClO_4$)		0.32		82CS	D
	sp	25	1.0 ($NaClO_4$)		0.40		82CS	D
	gl	25	0.1 ($NaClO_4$)	6.9	1.3		82DJ	T
	gl	30	0.1 ($NaClO_4$)	7.00	1.31		75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -5.4	ΔH_2 -2.5		82DJ	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	8.50	6.90		79LT	T
	gl	25	0.1 ($NaClO_4$)	0.14 (H_2L)			79LT	T
Al^{3+}	sp	25	0.1 ($NaClO_4$)	8.81			79LT	T
	gl	25	0.1 ($NaClO_4$)		6.58	4.34	79LT	T
Ga^{3+}	gl	25	0.2 ($NaClO_4$)	7.24	6.88	4.76	84MA	T
	gl	35	0.2 ($NaClO_4$)	7.24	6.57	3.86	84MA	T
	gl	45	0.2 ($NaClO_4$)	6.71	6.04	3.66	84MA	T
	T	35	0.2 ($NaClO_4$)	ΔH -25.9			84MA	T
	sp	15	0.2 ($NaClO_4$)	1.27 (HL^-)			82CS	T

cont'd

TABLE 28. 2-Hydroxy-3,5-dinitrobenzoic Acid $C_7H_4N_2O_7$ (continued)

	sp	25	0.2 ($NaClO_4$)	1.41 (HL^-)		82CS	T
	sp	35	0.2 ($NaClO_4$)	1.54 (HL^-)		82CS	T
	sp	45	0.2 ($NaClO_4$)	1.62 (HL^-)		82CS	T
VO^{2+}	gl	30	0.1 ($NaClO_4$)	6.96		77SJ	T
Mn^{2+}	gl	30	0.1 ($NaClO_4$)	3.06		75JK	T
Fe^{3+}	sp	25	1.0 ($NaClO_4$)	2.59 (HL^-)		82MSb	T
Co^{2+}	sp	25		3.82		83SG	Rj
	gl	30	0.1 ($NaClO_4$)	3.63		75JK	T
Ni^{2+}	sp	25	0.3 ($NaClO_4$)	3.75		87DS	T
	gl	25	0.3 ($NaClO_4$)	3.84		87DS	T
	gl	25	0.3 ($NaClO_4$)	K(M + HL = MHL)0.60		87DS	T
	sp	25		4.13		83SG	Rj
	gl	30	0.1 ($NaClO_4$)	4.11		75JK	T
Cu^{2+}	sp	?	?	6.68		81GS	Rj
	gl	30	0.1 ($NaClO_4$)	6.75	4.00	79SJ	T
	gl	30	0.05 ($NaClO_4$)	6.60	4.89	85AS	T
	gl	25	0.1 ($NaClO_4$)	6.8	5.0	82DJ	T
	gl	30	0.1 ($NaClO_4$)	6.70	3.95	75JK	T
	T	25	0.1 ($NaClO_4$)	ΔH_1 -16.7	ΔH_2 -10.5	82DJ	T
Zn^{2+}	gl	30	0.1 ($NaClO_4$)	3.32		75JK	T
Nd^{3+}	gl	30	0.1 ($NaClO_4$)	4.44		76SJ	T
UO_2^{2+}	gl	30	0.1 ($NaClO_4$)	6.39		77DS	T

TABLE 29. 2-Hydroxy-5-methyl-3-nitrobenzoic Acid $C_8H_7NO_5$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	?	20	0.1	10.80	2.78	80NS	D
Cu^{2+}	?	20	0.1	8.82		80NS	D
	?	30	0.1	8.94		80NS	D

3.6. Sulfo-substituted Salicylic Acids

3.6.1. 5-Sulfosalicylic Acid, $C_7H_5SO_6^-$, and 3,5-Disulfosalicylic Acid, $C_7H_3S_2O_9^{2-}$

Sulfo groups increase significantly the solubility of the parent compound. In aqueous solutions, the sulfonic acid group is a very strong acid, and practically quantitatively deprotonated. Sulfo groups (electron-widthdrawing groups) increase the acid strength of the OH- and COOH-groups (74SRa). In mixed aqueous solvents containing dioxan or ethanol, the lg K values of the OH- and COOH-groups are much larger than in aqueous solutions (79SJ, 85IS). The average values of the accepted

protonation constants for 5-sulfosalicylic acid in 0.1 - 0.2 M solution at 25 °C are $\lg(K_1/M^{-1}) = 11.67 \pm 0.20$ (T) and $\lg(K_2/M^{-1}) = 2.43 \pm 0.05$ (R).

The metal complex formation of 5-sulfosalicylic acid has been mostly studied with transition metal ions, and for instance, the Cu^{2+} complexes with 5-sulfosalicylic acid are widely studied.

The stability constants of 1:1 lanthanoid(III) complexes increase with increasing atomic number and show a tetrad effect (82DB). Entalpy and entropy changes involved in complex formation were determined on the basis of stability constants determined at three different temperatures. According to the H and S values obtained, these complexes could be divided roughly as two groups (La-Gd and Tb-Ho). The H and S values are strongly connected to the size of the hydration sphere of the lanthanoid(III) ions.

3,5-Disulfosalicylic acid forms strong complexes with Be^{2+}, Al^{3+}, Cu^{2+} ions and lanthanoid(III) ions. In the case of UO_2^{2+}, dinuclear complexes were also found to form. The ratio between the stepwise stability constants of the successive metal complexes of 3,5-disulfosalicylic acid is large due to the repulsion between the ionized sulfo groups of the ligand (76La, 78La).

Values of the stepwise stability constants are given in Tables 30 and 31.

TABLE 30. 2-Hydroxy-5-sulfobenzoic Acid $C_7H_6O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	30	0.1 (KNO_3)	11.42	2.68		79SV	T
	gl	30	0.1 ($NaClO_4$)	12.10	2.63		76SJ	T
	gl	25	0.12 NaCl	11.35	2.40		78RM	T
	gl	35	0.1 (KNO_3)	11.27	3.13		77JK	D
	cal	25	?		2.76		77AR	Rj
	cal	25	?		ΔH 3.50		77AR	Rj
	gl	25	0.2 (KNO_3)	11.86	2.43		79MB	T
	gl	25	0.1 ($NaClO_4$)	11.90	2.44		81C	T
	gl	20	0.1 (KNO_3)	12.04	2.40		82DB	T
	gl	30	0.1 (KNO_3)	11.81	2.37		82DB	T
	gl	40	0.1 (KNO_3)	11.52	2.35		82DB	T
	gl	25	0.1 (KNO_3)	11.67	2.32		80LM	T
	gl	25	0.1 ($NaClO_4$)		2.86	2.79	82AS	D
	gl	35	0.1 ($NaClO_4$)		3.19	3.02	82AS	D
	sp	?	?	11.77	2.87		81GS	Rj
	gl	25	0.5 ($NaClO_4$)	11.47	2.33	0.26	85CD	T
	sp	35	0.1 ($NaClO_4$)	11.90	2.44		79A	T
	gl	25	0.1 (KNO_3)	11.58	2.46		84RR	T
	gl	25	0.1 ($NaNO_3$)	11.45	2.46		82HN	T
	gl	25	1.0 ($NaClO_4$)	11.57	2.33		75SG	T
	gl	25	0.1 ($NaClO_4$)	11.87	2.47		74SRb	T
Be^{2+}	gl	35	0.1 (KNO_3)	11.11	9.32		77JK	T

cont'd

TABLE 30. 2-Hydroxy-5-sulfobenzoic Acid $C_7H_6O_6S$ (continued)

	gl	35	0.1 ($NaClO_4$)	11.61	8.95	84A	T
	gl	25	0.1 ($NaClO_4$)	11.74	8.92	74SRb	T
	gl	30	0.1 ($NaClO_4$)	9.70	5.90	83MS	D
	gl	35	0.1 ($NaClO_4$)	9.40	5.40	83MS	D
	gl	40	0.1 ($NaClO_4$)	9.20	5.20	83MS	D
	T	35	0.1 ($NaClO_4$)	ΔH -91.4		83MS	D
Mg^{2+}	gl	45	0.1 (KNO_3)	3.85		77TJ	T
	gl	25	0.1 ($NaNO_3$)	4.70		82HN	T
Ca^{2+}	gl	25	0.1 ($NaNO_3$)	3.07		82HN	T
Ba^{2+}	gl	25	0.1 ($NaNO_3$)	2.68		82HN	T
B^{3+}	gl	20	0.3 (KNO_3)	0.98 (HL^{2-})		78MB	T
	sp	25	0.1(NaCl)	0.85 (HL^{2-})		79QD	T
Al^{3+}	gl	25	0.5 ($NaClO_4$)	11.8	9.4	85CD	T
	sp	25	0.1 ($NaClO_4$)	0.88 (HL^{2-})		77PT	T
Ga^{3+}	gl	20	0.1 ($NaClO_4$)	12.70		85SA	T
	gl	25	0.1 (KNO_3)	12.50	10.0	80LM	T
In^{3+}	gl	20	0.1 ($NaClO_4$)	11.45		85SA	T
	gl	?	0.5	11.4		76KD	D
TiO^{2+}	pol	21	0.04 ($NaClO_4$)	$K(TiO^{2+} + HL^{2-} = Ti(OH)L)4.1$		77UB	T
	pol	21	0.6 ($NaClO_4$)	$K(Ti(OH)L+HL^{2-}=Ti(OH)L_2^{3-}+H)-0.2$		77UB	T
	pol	21	0.6 ($NaClO_4$)	$K(Ti(OH)L_2^{3-}+HL^{2-}=TiL_3^{5-}+H_2O)1.7$		77UB	T
VO^{2+}	gl	30	0.1 (KNO_3)	11.37		79SV	T
	gl	30	0.1 ($NaClO_4$)	11.71		77SJ	T
Cr^{3+}	gl	25	0.1 ($NaClO_4$)	10.50	8.30	81C	T
Mn^{2+}	gl	25	1.0 ($NaClO_4$)	4.77	3.42	75SG	T
Fe^{2+}	gl	25	0.1 ($NaClO_4$)	4.85	3.85	82AS	D
	gl	35	0.1 ($NaClO_4$)	5.05	3.90	82AS	D
	T	25	0.1 ($NaClO_4$)	ΔH 19.1		82AS	D
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	14.60		82C	T
	sp	24	0.2 ($NaClO_4$)	13.78	4.44	79DD	T
Co^{2+}	gl	45	0.1 (KNO_3)	5.62		77TJ	T
	ix	?	0.1 ($NaClO_4$)	6.8	3.02	79CP	D
	ix	?	0.1 ($NaClO_4$)	$K(M + HL = MHL)6.7$		79CP	D
	ix	?	0.1 ($NaClO_4$)	$K(MH_2L = ML + 2H)< 7$		79CP	D
	gl	25	0.1 ($NaClO_4$)	5.40	3.45	82AS	D
	gl	35	0.1 ($NaClO_4$)	5.65	3.75	82AS	D
	sp	25		6.12		83SG	Rj
	T	25	0.1 ($NaClO_4$)	ΔH 42.0		82AS	D
Ni^{2+}	gl	45	0.1 (KNO_3)	5.74		77TJ	T
	M	30	0.005	9.07		82LC	D
	ix	?	0.1 ($NaClO_4$)	6.4	3.84	79CP	D
	ix	?	0.1 ($NaClO_4$)	$K(M + HL = MHL)6.4$		79CP	D
	ix	?	0.1 ($NaClO_4$)	$K(MH_2L = ML + 2H)9.0$		79CP	D
	gl	25	0.1 ($NaClO_4$)	5.05	4.05	82AS	D
	gl	35	0.1 ($NaClO_4$)	5.20	4.30	82AS	D
	sp	25		6.14		83SG	Rj
	T	25	0.1 ($NaClO_4$)	ΔH 30.5		82AS	D

cont'd

TABLE 30. 2-Hydroxy-5-sulfobenzoic Acid $C_7H_6O_6S$ (continued)

Cu^{2+}	gl	30	0.1 ($NaClO_4$)	9.54	6.93	79SJ	T
	gl	25	0.12 NaCl	9.09		78RM	T
	gl	45	0.1 (KNO_3)	8.40		77TJ	T
	gl	25	0.2 (KNO_3)	9.57	7.05	79MB	T
	gl	25	0.1 ($NaClO_4$)	9.65	6.98	74SRb	T
	ix	?	0.1 ($NaClO_4$)	9.5	6.95	79CP	D
	ix	?	0.1 ($NaClO_4$)	K(M + HL = MHL)3.7		79CP	D
	ix	?	0.1 ($NaClO_4$)	K(MH_2L = ML + 2H)5.9		79CP	D
	gl	25	0.1 ($NaClO_4$)	5.36	4.10	82AS	D
	gl	35	0.1 ($NaClO_4$)	5.50	4.25	82AS	D
	T	25	0.1 ($NaClO_4$)	ΔH 22.9		82AS	D
	sp	?	?	8.96		81GS	Rj
	gl	35	0.1 ($NaClO_4$)	9.64	6.91	79A	T
Zn^{2+}	gl	25	0.12 NaCl	< 2 (HL^{2-})		78RM	D
	gl	30	0.1 ($NaClO_4$)	7.95	6.25	82MSa	T
	gl	35	0.1 ($NaClO_4$)	7.70	5.85	82MSa	T
	gl	40	0.1 ($NaClO_4$)	7.20	5.60	82MSa	T
	T	30	0.1 ($NaClO_4$)	ΔH -137.1		82MSa	T
Sc^{3+}	gl	20	0.1 ($NaClO_4$)	11.23		85SA	T
Y^{3+}	gl	20	0.1 (KNO_3)	7.92		82DB	T
	gl	30	0.1 (KNO_3)	7.50		82DB	T
	gl	40	0.1 (KNO_3)	7.42		82DB	T
	gl	20	0	9.32		82DB	T
	T	20	0.1 (KNO_3)	ΔH -43.3		82DB	T
La^{3+}	gl	20	0.1 (KNO_3)	7.24		82DB	T
	gl	30	0.1 (KNO_3)	6.43		82DB	T
	gl	40	0.1 (KNO_3)	6.22		82DB	T
	gl	20	0	8.94		82DB	T
	T	20	0.1 (KNO_3)	ΔH -90.1		82DB	T
Ce^{3+}	gl	20	0.1 (KNO_3)	7.40		82DB	T
	gl	30	0.1 (KNO_3)	6.95		82DB	T
	gl	40	0.1 (KNO_3)	6.62		82DB	T
	gl	20	0	9.00		82DB	T
	T	20	0.1 (KNO_3)	ΔH -70.7		82DB	T
Pr^{3+}	gl	20	0.1 (KNO_3)	7.55		82DB	T
	gl	30	0.1 (KNO_3)	7.13		82DB	T
	gl	40	0.1 (KNO_3)	6.88		82DB	T
	gl	20	0	9.07		82DB	T
	T	20	0.1 (KNO_3)	ΔH -61.3		82DB	T
Nd^{3+}	gl	30	0.1 ($NaClO_4$)	7.39	5.62	76SJ	T
	sp	25	1.0	6.76		77KT	T
	gl	20	0.1 (KNO_3)	7.71		82DB	T
	gl	30	0.1 (KNO_3)	7.25		82DB	T
	gl	40	0.1 (KNO_3)	7.03		82DB	T
	gl	20	0	9.19		82DB	T
	T	20	0.1 (KNO_3)	ΔH -60.0		82DB	T
Sm^{3+}	gl	25	1.0 ($NaClO_4$)	6.339	5.682	82DB	T
	gl	20	0.1 (KNO_3)	7.99		82DB	T

cont'd

TABLE 30. 2-Hydroxy-5-sulfobenzoic Acid $C_7H_6O_6S$ (continued)

	gl	30	0.1 (KNO_3)	7.75		82DB	T
	gl	40	0.1 (KNO_3)	7.37		82DB	T
	gl	20	0	9.44		82DB	T
	T	20	0.1 (KNO_3)	ΔH -54.7		82DB	T
Eu^{3+}	gl	25	1.0 ($NaClO_4$)	6.267	5.488	79NC	T
Gd^{3+}	gl	20	0.1 (KNO_3)	7.78		82DB	T
	gl	30	0.1 (KNO_3)	7.61		82DB	T
	gl	40	0.1 (KNO_3)	7.22		82DB	T
	gl	20	0	9.20		82DB	T
	T	20	0.1 (KNO_3)	ΔH -50.7		82DB	T
Tb^{3+}	gl	20	0.1 (KNO_3)	7.80		82DB	T
	gl	30	0.1 (KNO_3)	7.73		82DB	T
	gl	40	0.1 (KNO_3)	7.57		82DB	T
	gl	20	0	9.26		82DB	T
	T	20	0.1 (KNO_3)	ΔH -22.4		82DB	T
Dy^{3+}	gl	20	0.1 (KNO_3)	7.98		82DB	T
	gl	30	0.1 (KNO_3)	7.83		82DB	T
	gl	40	0.1 (KNO_3)	7.69		82DB	T
	gl	20	0	9.28		82DB	T
	T	20	0.1 (KNO_3)	ΔH -26.4		82DB	T
Ho^{3+}	gl	20	0.1 (KNO_3)	8.13		82DB	T
	gl	30	0.1 (KNO_3)	8.09		82DB	T
	gl	40	0.1 (KNO_3)	7.81		82DB	T
	gl	20	0	9.61		82DB	T
	T	20	0.1 (KNO_3)	ΔH -27.6		82DB	T
Th^{4+}	gl	20	0.1 ($NaClO_4$)	11.97		85SA	T
UO_2^{2+}	gl	30	0.1 ($NaClO_4$)	11.14		77DS	T
	ix	?	0.1 ($NaClO_4$)	11.0	8.20	79CP	D
	ix	?	0.1 ($NaClO_4$)	K(M + HL = MHL)2.1		79CP	D
	ix	?	0.1 ($NaClO_4$)	K(MH_2L = ML + 2H)5.85		79CP	D
NpO_2^+	sp	25	2.0 ($NaClO_4$)	0.17		90RN	T
Pu^{3+}	gl	25	1.0 ($NaClO_4$)	8.574	8.940	79NC	T
Am^{3+}	gl	25	1.0 ($NaClO_4$)	8.059	7.283	79NC	T

TABLE 31. 2-Hydroxy-3,5-disulfobenzoic Acid $C_7H_6O_9S_2$

Metal	Method	t/°C	I_c/M	lg(K_1/M^{-1})	lg(K_2/M^{-1})	Reference	Category
H^+	gl	25	0	12.50	2.69	75L	T
	gl	25	0.5 ($NaClO_4$)	11.07	1.70	74SRa	T
Be^{2+}	gl	25	0.5 ($NaClO_4$)	10.50	8.19	74SRa	T
Al^{3+}	gl	25	0.5 ($NaClO_4$)	11.507	8.68	78La	T
Cu^{2+}	gl	25	0	11.49		75L	T
	gl	25	0.5 ($NaClO_4$)	9.13	7.00	74SRa	T

cont'd

TABLE 31. 2-Hydroxy-3,5-disulfobenzoic Acid $C_7H_6O_9S_2$ (continued)

Y^{3+}	gl	25	0.5 ($NaClO_4$)	8.64	5.74	76Lb	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 12.7		76Lb	T
Pr^{3+}	gl	25	0.5 ($NaClO_4$)	7.66	5.06	76La	T
Nd^{3+}	gl	25	0.5 ($NaClO_4$)	7.77	5.11	76La	T
Sm^{3+}	gl	25	0.5 ($NaClO_4$)	8.20	5.34	76La	T
Eu^{3+}	gl	25	0.5 ($NaClO_4$)	8.35	5.41	76La	T
Gd^{3+}	gl	25	0.5 ($NaClO_4$)	8.59	5.56	76La	T
Tb^{3+}	gl	25	0.5 ($NaClO_4$)	8.74	5.68	76La	T
Dy^{3+}	gl	25	0.5 ($NaClO_4$)	8.82	5.72	76La	T
Ho^{3+}	gl	25	0.5 ($NaClO_4$)	8.77	5.82	76La	T
Er^{3+}	gl	25	0.5 ($NaClO_4$)	8.81	5.83	76La	T
Tm^{3+}	gl	25	0.5 ($NaClO_4$)	8.85	5.85	76La	T
Yb^{3+}	gl	25	0.5 ($NaClO_4$)	8.90	5.99	76La	T
Lu^{3+}	gl	25	0.5 ($NaClO_4$)	8.86	5.99	76La	T
UO_2^{2+}	gl	25	0.5 ($NaClO_4$)	10.774	7.672	79LS	T
	gl	25	0.5 ($NaClO_4$)	β_{201} 13.068		79LS	T
	gl	25	0.5 ($NaClO_4$)	$\beta_{1\text{-}11}$ 4.205		79LS	T
	gl	25	0.5 ($NaClO_4$)	$\beta_{1\text{-}12}$ 11.366		79LS	T

3.6.2. Bromo-, Mercurio- and Methyl-substituted Sulfosalicylic Acids, $C_7H_4BrSO_6^-$, $C_7H_4HgSO_6^-$, $C_8H_7SO_6^-$

In 3-bromo-5-sulfosalicylic acid, both the substituents, the Br- and SO_3-groups, increase the acidity of the hydroxyl and carboxyl group. In Fe^{3+} complex formation with 3-mercurio-5-sulfosalicylic acid, a bathochromic effect has been observed in the corresponding absorption spectra due to the mercury atom. As a consequence of complex formation, hypsochromic effects are usually noted in the absorption spectra when the ligand contains electron-widthdrawing substituents, like nitro- and sulfo-groups. In general, the metal complexes of methylsulfosalicylic are more stable than those of 5-sulfosalicylic acid (Tables 32 - 36).

TABLE 32. 3-Bromo-2-hydroxy-5-sulfobenzoic Acid $C_7H_5BrO_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	3.0 ($NaClO_4$)	10.467	2.028		76Ld	T
	gl	25	0.1 ($NaClO_4$)	10.52	2.02		92AL	T
	cal	25	0.1 ($NaClO_4$)	ΔH -1.2			93AL	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	10.31	7.45		92AL	T

cont'd

TABLE 32. 3-Bromo-2-hydroxy-5-sulfobenzoic Acid $C_7H_5BrO_6S$ (continued)

Al^{3+}	gl	25	0.1 ($NaClO_4$)	11.32	8.78	5.43	92AL	T
Pb^{2+}	gl	25	3.0 ($NaClO_4$)	β_{111} 1.116 (HL^{2-})			76Le	T
	gl	25	3.0 ($NaClO_4$)	β_{122} 1.931 (HL^{2-})			76Le	T
	gl	25	3.0 ($NaClO_4$)	β_{101} -4.875 (HL^{2-})			76Le	T
	gl	25	3.0 ($NaClO_4$)	β_{102} -11.187 (HL^{2-})			76Le	T
La^{3+}	gl	25	0.1 ($NaClO_4$)	6.49	4.23		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.30			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-11} -2.73			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -11.85			93AL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 2.2			93AL	T
Pr^{3+}	gl	25	0.1 ($NaClO_4$)	6.84	4.86		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.34			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-11} -1.75			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -10.31			93AL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 0.9			93AL	T
Nd^{3+}	gl	25	0.1 ($NaClO_4$)	6.86	4.75		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.36			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-11} -1.16			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -9.70			93AL	T
Sm^{3+}	gl	25	0.1 ($NaClO_4$)	7.39	5.00		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.48			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-11} -0.35			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -8.18			93AL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 2.3			93AL	T
Eu^{3+}	gl	25	0.1 ($NaClO_4$)	7.60	5.42		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.46			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-11} -0.09			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -8.49			93AL	T
Gd^{3+}	gl	25	0.1 ($NaClO_4$)	7.40	4.95		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.38			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-11} -0.54			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -9.22			93AL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 3.8			93AL	T
Tb^{3+}	gl	25	0.1 ($NaClO_4$)	7.47	5.14		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.42			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -8.25			93AL	T
Dy^{3+}	gl	25	0.1 ($NaClO_4$)	7.58	5.27		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.28			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -8.42			93AL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 4.6			93AL	T
Ho^{3+}	gl	25	0.1 ($NaClO_4$)	7.64	5.45		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.38			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-21} -7.71			93AL	T
Er^{3+}	gl	25	0.1 ($NaClO_4$)	7.72	5.47		93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.30			93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{1-11} 0.36			93AL	T

cont'd

TABLE 32. 3-Bromo-2-hydroxy-5-sulfobenzoic Acid $C_7H_5BrO_6S$ (continued)

	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}21}$ -7.17		93AL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 2.2		93AL	T
Tm^{3+}	gl	25	0.1 ($NaClO_4$)	7.69	5.55	93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.34		93AL	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}21}$ -7.15		93AL	T
Yb^{3+}	gl	25	0.1 ($NaClO_4$)	7.83	5.83	93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.39		93AL	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}21}$ -6.40		93AL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 3.9		93AL	T
Lu^{3+}	gl	25	0.1 ($NaClO_4$)	7.56	5.86	93AL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 12.33		93AL	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}11}$ 0.42		93AL	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}21}$ -6.85		93AL	T
UO_2^{2+}	gl	25	0.1 ($NaClO_4$)	10.35	7.39	92AL	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}12}$ 8.4		92AL	T

TABLE 33. 2-Hydroxy-3-mercurio-5-sulfobenzoic Acid $C_7H_5HgO_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	0.1 ($NaClO_4$)	12.03	2.43	82C	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	15.10		82C	T

TABLE 34. 2-Hydroxy-5-methyl-3-sulfobenzoic Acid $C_8H_8O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	0.1 ($NaClO_4$)	13.47	2.52	82C	T
	gl	35	0.1 ($NaClO_4$)	13.47	2.52	81AS	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	12.54	9.07	81CS	T
	gl	35	0.1 ($NaClO_4$)	12.75	9.00	84A	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	16.34		82C	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	10.71	6.97	81CS	T
	gl	35	0.1 ($NaClO_4$)	10.70	6.60	81AS	T

TABLE 35. 2-Hydroxy-4-methyl-5-sulfobenzoic Acid $C_8H_8O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	0.1 ($NaClO_4$)	12.33	2.67	82C	T
	gl	35	0.1 ($NaClO_4$)	12.33	2.68	81AS	T
Be^{2+}	gl	35	0.1 ($NaClO_4$)	12.72	9.25	84A	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	15.23		82C	T
Cu^{2+}	gl	35	0.1 ($NaClO_4$)	9.98	7.26	81AS	T

TABLE 36. 2-Hydroxy-3-methyl-5-sulfobenzoic Acid $C_8H_8O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	25	0.1 ($NaClO_4$)	12.58	2.89	81C	T
	sp	25	0.1 ($NaClO_4$)	12.58	2.54	82C	T
	gl	35	0.1 ($NaClO_4$)	12.58	2.54	81AS	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	12.12	8.96	81CS	T
	gl	35	0.1 ($NaClO_4$)	12.04	8.99	84A	T
Cr^{3+}	gl	25	0.1 ($NaClO_4$)	11.15	8.60	81C	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	15.34		82C	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	9.74	6.71	81CS	T
	gl	35	0.1 ($NaClO_4$)	9.85	6.62	81AS	T

3.6.3. 5-(4-Sulfophenylazo)salicylic Acid, $C_{13}H_9N_2SO_6^-$, 4-Methyl-5-(4-sulfophenylazo)salicylic Acid, $C_{14}H_{11}N_2SO_6^-$, and 5-(3-Nitro-4-sulfophenylazo)-salicylic Acid, $C_{13}H_8N_3SO_8^-$

Only two papers are available on protonation and complex formation of these ligand acids, and due to the inadequate data, the values given should be rejected (Tables 37 - 39).

TABLE 37. 2-Hydroxy-5-(4-sulfophenylazo)benzoic Acid $C_{13}H_{10}N_2O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	?	11.26	2.26	81GS	Rj
Co^{2+}	sp	25	?	6.01		82GS	Rj
Ni^{2+}	sp	25	?	6.23		82GS	Rj
Cu^{2+}	sp	25	?	9.11		81GS	Rj

TABLE 38. 2-Hydroxy-4-methyl-5-(4-sulfophenylazo)benzoic Acid $C_{14}H_{12}N_2O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	?	11.45	2.45	81GS	Rj
Co^{2+}	sp	25	?	5.54		82GS	Rj
Ni^{2+}	sp	25	?	6.39		82GS	Rj
Cu^{2+}	sp	25	?	10.31		81GS	Rj

TABLE 39. 2-Hydroxy-5-(3-nitro-4-sulfophenylazo)benzoic Acid $C_{13}H_9N_3O_8S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	25	?	11.15	2.16	81GS	Rj
Co^{2+}	sp	25	?	6.03		82GS	Rj
Ni^{2+}	sp	25	?	6.88		82GS	Rj
Cu^{2+}	sp	25	?	10.14		81GS	Rj

3.7. Aminosalicylic Acids, $C_7H_7NO_3$

Amino groups diminish the basicity of salicylic acid, which is shown in the decreased stability of the corresponding metal complexes (79LKa). However, the effect is not so significant as it is in the case of nitro groups. The acidity of substituted salicylic acids increase in the following order: 3-methylsalicylic acid < salicylic acid < 4-aminosalicylic acid < 3-nitrosalicylic acid < 3,5-dinitrosalicylic acid (89K).

The most studied of these ligand acids is 5-aminosalicylic acid (Table 40) due to the poor solubility of the other aminosalicylic acids.

The complex equilibria of the Be^{2+} - 5-aminosalicylic acid system is very complicated, in which protonated (BeHL dominating at pH < 5), "normal" mononuclear (BeL dominating at 5.5 < pH 7), and hydrolyzed species (Be(OH)L dominating at pH > 7) were found to form. In addition, the data also indicate formation of binuclear complex species (79LKa).

TABLE 40. 5-Amino-2-hydroxybenzoic Acid $C_7H_7NO_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	0.5 ($NaClO_4$)	11.535	5.604	2.280	79LKa	T

cont'd

TABLE 40. 5-Amino-2-hydroxybenzoic Acid $C_7H_7NO_3$ (continued)

	sp	35	0.1 ($NaClO_4$)	15.95	3.01		79A	D
	gl	37	0.150 (Cl^-)	12.54	5.33	2.00	93WW	T
Be^{2+}	gl	25	0.5 ($NaClO_4$)	10.768	6.762		79LKa	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 16.121			79LKa	T
	gl	25	0.5 ($NaClO_4$)	β_{211} 19.478			79LKa	T
	gl	25	0.5 ($NaClO_4$)	β_{201} 15.567			79LKa	T
	gl	25	0.5 ($NaClO_4$)	β_{302} 28.2			79LKa	T
	gl	25	0.5 ($NaClO_4$)	β_{1-11} 3.752			79LKa	T
	gl	30	0.1 ($NaClO_4$)	14.40	6.90		83MS	T
	gl	35	0.1 ($NaClO_4$)	14.10	6.00		83MS	T
	gl	40	0.1 ($NaClO_4$)	13.90	6.50		83MS	T
	T	35	0.1 ($NaClO_4$)	ΔH -91.4			83MS	T
B^{3+}	gl	20	0.1 (KNO_3)	1.31 (HL^-)			78MB	T
Fe^{3+}	sp	37	0.150 (Cl^-)	β_{121} 21.83			93WW	T
Co^{2+}	gl	37	0.150 (Cl^-)	4.44			93WW	T
	gl	37	0.150 (Cl^-)	β_{1-11} -2.15			93WW	T
Cu^{2+}	gl	35	0.1 ($NaClO_4$)	12.18	9.73		79A	D
	gl	37	0.150 (Cl^-)	10.63			93WW	T
	gl	37	0.150 (Cl^-)	β_{111} 15.57			93WW	T
Zn^{2+}	gl	30	0.1 ($NaClO_4$)	8.85	6.35		82MSa	T
	gl	35	0.1 ($NaClO_4$)	8.80	5.90		82MSa	T
	gl	40	0.1 ($NaClO_4$)	8.60	5.00		82MSa	T
	T	30	0.1 ($NaClO_4$)	ΔH -45.7			82MSa	T
	gl	37	0.150 (Cl^-)	β_{1-11} -0.95			93WW	T

3.8. Cyanosalicylic Acids, $C_8H_5NO_3$

Only a few papers deal with protonation and complex formation of cyano-substituted salicylic acids (Table 41). The effect of the substituent is similar to that of the amino group (79A, 89YA).

TABLE 41. 5-Cyano-2-hydroxybenzoic Acid $C_8H_5NO_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	sp	35	0.1 ($NaClO_4$)	10.65	2.00	79A	D
	sp	25	(NaClO4)	11.301	2.34	89YA	T
Cu^{2+}	gl	35	0.1 ($NaClO_4$)	8.89	6.56	79A	D
UO_2^{2+}	sp	25	($NaClO_4$)	11.03 (L^{2-})		89YA	D
	sp	25	($NaClO_4$)	1.73 (HL^-)		89YA	D
	sp	25	($NaClO_4$)	-2.60 (H_2L)		89YA	D

3.9. *ortho*-Hydroxynaphthoic Acids, $C_{11}H_8O_3$

The solubility of *ortho*-hydroxynaphthoic acids in water is very limited, and only some papers deal with protonation or complex formation of these ligand acids (Tables 42 - 44). Most of the studies are carried out in 50% water-ethanol mixtures. Some reference books give the values $\lg(K_1/M^{-1}) = 14.00$ and $\lg(K_2/M^{-1}) = 4.16$ for the protonation constants of 1-hydroxy-2-naphthoic acid (70SS). These values, however, deviate significantly from those reported in reference 87PB.

TABLE 42. 1-Hydroxy-2-naphthoic Acid $C_{11}H_8O_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
B^{3+}	gl	20	0.1 (KNO_3)	1.31 (HL^-)		78MB	T
Zn^{2+}	gl	30	0.1 (KNO_3)	7.49	6.85	76SS	T
Y^{3+}	gl	30	0.1 (KNO_3)	8.76	8.29	76SS	T
Cd^{2+}	gl	30	0.1 (KNO_3)	6.68	5.75	76SS	T
Hg^{2+}	gl	30	0.1 (KNO_3)		0.89	76SS	T
La^{3+}	gl	30	0.1 (KNO_3)	8.32	7.62	76SS	T
Ce^{3+}	gl	30	0.1 (KNO_3)	8.63	7.57	76SS	T

TABLE 43. 2-Hydroxy-1-naphthoic Acid $C_{11}H_8O_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	Reference	Category
B^{3+}	gl	20	0.1 (KNO_3)	1.83 (HL^-)	78MB	T

TABLE 44. 2-Hydroxy-3-naphthoic Acid $C_{11}H_8O_3$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	25	0	11.75	3.90	77DC	D
	gl	20	0.1 (KNO_3)	11.52	2.78	77SK	T
B^{3+}	gl	20	0.1 (KNO_3)	1.29 (HL^-)		78MB	T
Al^{3+}	sp	?	?	13.19		77GG	Rj
Cu^{2+}	gl	25	0	9.10		77DC	D
Y^{3+}	gl	20	0.1 (KNO_3)	8.70	8.37	77SK	T
La^{3+}	gl	20	0.1 (KNO_3)	8.51	7.78	77SK	T
Ce^{3+}	gl	20	0.1 (KNO_3)	8.67	7.87	77SK	T

3.10. Sulfo-substituted *ortho*-Hydroxynaphthoic Acids

Only two research groups have studied protonation and metal complex formation of these ligand acids. The most studied metal ions are Be^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+}, and trivalent lanthanoid ions (Tables 45 - 53).

TABLE 45. 1-Hydroxy-4-sulfo-2-naphthoic Acid $C_{11}H_8O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	0.1 ($NaClO_4$)	11.650	2.502		78Lb	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	11.186	8.87		78Lb	T
Al^{3+}	gl	25	0.1 ($NaClO_4$)	12.102	9.259	7.699	81LAc	T
	sp	25	0.1 ($NaClO_4$)	12.640			81LAc	T
	sp	25	0.1 ($NaClO_4$)	12.64			88LK	T
	gl	25	0.1 ($NaClO_4$)		9.25		88LK	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}12}$ 13.98			88LK	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}22}$ 5.32			88LK	T
Fe^{3+}	gl	25	0.1 ($NaClO_4$)		10.88	7.37	79LP	T
	sp	25	0.1 ($NaClO_4$)	14.037	10.975	7.338	79LP	T
	gl	25	0.1 ($NaClO_4$)	15.85	10.96	7.24	81LAa	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	9.837	6.67		78Lb	T
La^{3+}	gl	25	0.1 ($NaClO_4$)	7.081	5.060		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.11			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.46 (HL^{2-})			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.05 (HL^{2-})			88LL	T
Ce^{3+}	gl	25	0.1 ($NaClO_4$)	7.337	5.123		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.06			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.41 (HL^{2-})			79LE	T
Pr^{3+}	gl	25	0.1 ($NaClO_4$)	7.412	5.150		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.34			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.69 (HL^{2-})			79LE	T
Nd^{3+}	gl	25	0.1 ($NaClO_4$)	7.437	5.163		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.77			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.12 (HL^{2-})			79LE	T
Sm^{3+}	gl	25	0.1 ($NaClO_4$)	8.284	6.025		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.861			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.21 (HL^{2-})			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.43 (HL^{2-})			88LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 2.29			88LL	T
Eu^{3+}	gl	25	0.1 ($NaClO_4$)	8.694	6.236		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 14.211			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.56 (HL^{2-})			79LE	T
Gd^{3+}	gl	25	0.1 ($NaClO_4$)	8.461	6.309		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 14.158			79LE	T

cont'd

TABLE 45. 1-Hydroxy-4-sulfo-2-naphthoic Acid $C_{11}H_8O_6S$ (continued)

	gl	25	0.1 ($NaClO_4$)	β_{111} 2.51 (HL^{2-})			79LE	T
Tb^{3+}	gl	25	0.1 ($NaClO_4$)	8.806	6.158		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.99			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.34 (HL^{2-})			79LE	T
Dy^{3+}	gl	25	0.1 ($NaClO_4$)	8.872	6.281		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.843			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.19 (HL^{2-})			79LE	T
Ho^{3+}	gl	25	0.1 ($NaClO_4$)	8.822	6.350		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.751			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.10 (HL^{2-})			79LE	T
Er^{3+}	gl	25	0.1 ($NaClO_4$)	8.877	6.593		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.66			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.01 (HL^{2-})			79LE	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 6.11			88LL	T
Tm^{3+}	gl	25	0.1 ($NaClO_4$)	8.864	6.656		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.53			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.88 (HL^{2-})			79LE	T
Yb^{3+}	gl	25	0.1 ($NaClO_4$)	8.829	6.851		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.48			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.83 (HL^{2-})			79LE	T
Lu^{3+}	gl	25	0.1 ($NaClO_4$)	8.807	6.873		79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 13.42			79LE	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.82 (HL^{2-})			79LE	T
UO_2^{2+}	gl	25	0.1 ($NaClO_4$)	11.247	8.421	4.558	81LAc	T
	sp	25	0.1 ($NaClO_4$)	11.773			81LAc	T
	sp	25	0.1 ($NaClO_4$)	11.77			88LK	T
	gl	25	0.1 ($NaClO_4$)		9.01		88LK	T
	gl	25	0.1 ($NaClO_4$)	β_{1-12} 10.86			88LK	T

TABLE 46. 1-Hydroxy-7-sulfo-2-naphthoic Acid $C_{11}H_8O_6S$

Metal	Method	t/°C	I_c/M	lg(K_1/M^{-1})	lg(K_2/M^{-1})	lg(K_3/M^{-1})	Reference	Category
H^+	gl	25	0.1 ($NaClO_4$)	12.374	2.723		80LH	T
	sp	25	0.1 ($NaClO_4$)	12.365	2.729		80LH	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	11.847	8.666		80LH	T
	sp	25	0.1 ($NaClO_4$)	12.228	8.622		80LH	T
Al^{3+}	sp	25	0.1 ($NaClO_4$)	13.88			88LK	T
	gl	25	0.1 ($NaClO_4$)		9.64		88LK	T
	gl	25	0.1 ($NaClO_4$)	β_{1-12} 15.22			88LK	T
	gl	25	0.1 ($NaClO_4$)	β_{1-22} 6.54			88LK	T
	gl	25	0.1 ($NaClO_4$)	13.884	11.625	5.040	81LAc	T
	sp	25	0.1 ($NaClO_4$)	13.884			81LAc	T

cont'd

TABLE 46. 1-Hydroxy-7-sulfo-2-naphthoic Acid $C_{11}H_8O_6S$ (continued)

Fe^{3+}	gl	25	0.1 ($NaClO_4$)		10.958	7.238	81LAa	T
	sp	25	0.1 ($NaClO_4$)	15.853	11.58	6.677	81LAa	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	10.209	6.403		80LH	T
	sp	25	0.1 ($NaClO_4$)	10.714	6.163		80LH	T
	sp	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}12}$ 7.872			80LH	T
UO_2^{2+}	sp	25	0.1 ($NaClO_4$)	13.35			88LK	T
	gl	25	0.1 ($NaClO_4$)	12.82	8.60		88LK	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}11}$ 5.92			88LK	T
	gl	25	0.1 ($NaClO_4$)	$\beta_{1\text{-}12}$ 11.69			88LK	T
	gl	25	0.1 ($NaClO_4$)	12.823	8.596	5.551	81LAc	T
	sp	25	0.1 ($NaClO_4$)	13.351			81LAc	T

TABLE 47. 1-Hydroxy-4,7-disulfo-2-naphthoic Acid $C_{11}H_8O_9S_2$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	0.5 ($NaClO_4$)	10.788	2.233		78LT	T
	gl	25	0.1 ($NaClO_4$)	11.119	2.208		81LAa	T
	cal	25	0.1 ($NaClO_4$)	ΔH -1.7			86LL	T
Be^{2+}	gl	25	0.5 ($NaClO_4$)	10.495	8.20		78LT	T
Al^{3+}	gl	25	0.5 ($NaClO_4$)	12.379	8.600	5.793	81LAc	T
	sp	25	0.5 ($NaClO_4$)	12.379			81LAc	T
	sp	25	0.5($NaClO_4$)	12.38			88LK	T
	gl	25	0.5 ($NaClO_4$)		9.17		88LK	T
	gl	25	0.5 ($NaClO_4$)	$\beta_{1\text{-}12}$ 13.66			88LK	T
Fe^{3+}	gl	25	0.1 ($NaClO_4$)		9.714		81LAa	T
	sp	25	0.1 ($NaClO_4$)	14.686	10.054		81LAa	T
Cu^{2+}	gl	25	0.5 ($NaClO_4$)	9.390	6.40		78LT	T
La^{3+}	gl	25	0.1 ($NaClO_4$)	7.08	4.6		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.01 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 4.2			86LL	T
Pr^{3+}	gl	25	0.1 ($NaClO_4$)	7.61	5.1		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.06 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 2.1			86LL	T
Nd^{3+}	gl	25	0.1 ($NaClO_4$)	7.85	4.6		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.07 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 2.6			86LL	T
Sm^{3+}	gl	25	0.1 ($NaClO_4$)	8.49	5.7		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.25 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 2.9			86LL	T
Eu^{3+}	gl	25	0.1 ($NaClO_4$)	8.71	5.9		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.22 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 4.0			86LL	T

cont'd

TABLE 47. 1-Hydroxy-4,7-disulfo-2-naphthoic Acid $C_{11}H_8O_9S_2$ (continued)

Gd^{3+}	gl	25	0.1 ($NaClO_4$)	8.67	5.8		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.06 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 7.0			86LL	T
Tb^{3+}	gl	25	0.1 ($NaClO_4$)	8.85	5.9		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.94 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 6.2			86LL	T
Dy^{3+}	gl	25	0.1 ($NaClO_4$)	8.95	5.8		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.89 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 6.7			86LL	T
Ho^{3+}	gl	25	0.1 ($NaClO_4$)	8.86	5.8		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.92 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 8.4			86LL	T
Er^{3+}	gl	25	0.1 ($NaClO_4$)	8.86	5.8		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.88 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH 9.2			86LL	T
Tm^{3+}	gl	25	0.1 ($NaClO_4$)	9.01	5.8		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.95 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 8.1			86LL	T
Yb^{3+}	gl	25	0.1 ($NaClO_4$)	8.91	5.7		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.90 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 7.7			86LL	T
Lu^{3+}	gl	25	0.1 ($NaClO_4$)	8.80	5.7		86LL	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 1.99 (HL^{3-})			86LL	T
	cal	25	0.1 ($NaClO_4$)	ΔH_{111} 7.5			86LL	T
UO_2^{2+}	gl	25	0.5 ($NaClO_4$)	10.935	7.894	3.404	81LAc	T
	sp	25	0.5 ($NaClO_4$)	11.019			81LAc	T
	gl	25	0.5 ($NaClO_4$)	10.935	7.894	3.40	88LK	T
	sp	25	0.5 ($NaClO_4$)	11.02			88LK	T

TABLE 48. 3-Hydroxy-4-sulfo-2-naphthoic Acid $C_{11}H_8O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	25	0.1 ($NaClO_4$)	11.35	2.46	76Lc	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	11.19	8.62	76Lc	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	9.40	6.61	76Lc	T

TABLE 49. 3-Hydroxy-5-sulfo-2-naphthoic Acid $C_{11}H_8O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H^+	gl	25	0.1 ($NaClO_4$)	11.49	2.39	74SRb	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	11.05	7.89	74SRb	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	8.88	5.79	74SRb	T

TABLE 50. 3-Hydroxy-7-sulfo-2-naphthoic Acid $C_{11}H_8O_6S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	sp	25	0.1 KCl	11.92	2.53		80LP	T
	gl	25	0.1 ($NaClO_4$)	11.73	2.44		74SRb	T
Be^{2+}	gl	25	0.1 ($NaClO_4$)	11.15	8.41		74SRb	T
Al^{3+}	gl	25	0.1 ($NaClO_4$)	11.894	9.24	7.92	80LP	T
	sp	25	0.1 ($NaClO_4$)	11.932			80LP	T
	sp	25	0.1 KCl	11.316			80LP	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	14.567	10.67	8.34	81LAb	T
Cu^{2+}	gl	25	0.1 ($NaClO_4$)	8.89	6.33		74SRb	T
Nd^{3+}	gl	25	0.1 ($NaClO_4$)	6.82			76ML	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.07 (HL^{2-})			76ML	T
Sm^{3+}	gl	25	0.1 ($NaClO_4$)	7.44			76ML	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.31 (HL^{2-})			76ML	T
Eu^{3+}	gl	25	0.1 ($NaClO_4$)	7.79			76ML	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.65 (HL^{2-})			76ML	T
Gd^{3+}	gl	25	0.1 ($NaClO_4$)	7.73			76ML	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.62 (HL^{2-})			76ML	T
Tb^{3+}	gl	25	0.1 ($NaClO_4$)	7.71			76ML	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.44 (HL^{2-})			76ML	T
Dy^{3+}	gl	25	0.1 ($NaClO_4$)	7.68			76ML	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.32 (HL^{2-})			76ML	T
Ho^{3+}	gl	25	0.1 ($NaClO_4$)	7.62			76ML	T
	gl	25	0.1 ($NaClO_4$)	β_{111} 2.21 (HL^{2-})			76ML	T

TABLE 51. 3-Hydroxy-5,7-disulfo-2-naphthoic Acid $C_{11}H_8O_9S_2$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	0.5 ($NaClO_4$)	10.92	2.14		74SRa	T
	gl	25	0	12.03	2.98		75L	T

cont'd

TABLE 51. 3-Hydroxy-5,7-disulfo-2-naphthoic Acid $C_{11}H_8O_9S_2$ (continued)

Be^{2+}	gl	25	0.5 ($NaClO_4$)	10.18	7.99		74SRa	T
Al^{3+}	gl	25	0.5 ($NaClO_4$)	10.812	8.45		78La	T
Fe^{3+}	sp	25	0.1 ($NaClO_4$)	14.052	9.72	8.26	81LAb	T
Cu^{2+}	gl	25	0.5 ($NaClO_4$)	8.18	5.93		74SRa	T
	gl	25	0	10.29			75L	T
Y^{3+}	gl	25	0.5 ($NaClO_4$)	6.465	5.385		80LK	T
	gl	25	0.5 ($NaClO_4$)	$\beta_{1\text{-}11}$ -1.327			80LK	T
	gl	25	0.5 ($NaClO_4$)	$\beta_{1\text{-}12}$ 3.57			80LK	T
UO_2^{2+}	gl	25	0.5 ($NaClO_4$)	9.809	7.59		78LKb	T

TABLE 52. 1,7-Dihydroxy-4-sulfo-2-naphthoic Acid $C_{11}H_8O_7S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	sp	25	0.5 ($NaClO_4$)	12.254	8.810	2.684	82LK	T
	gl	25	0.5 ($NaClO_4$)	11.93	8.876	2.663	82LK	T
Be^{2+}	gl	25	0.5 ($NaClO_4$)	14.43	6.424		82LK	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 20.327			82LK	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 30.11			82LK	T
	gl	25	0.5 ($NaClO_4$)	β_{122} 38.762			82LK	T
Al^{3+}	gl	25	0.5 ($NaClO_4$)	14.952	7.188	6.07	82LK	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 20.001			82LK	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 30.80			82LK	T
Cu^{2+}	gl	25	0.5 ($NaClO_4$)	11.79	5.628		82LK	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 18.576			82LK	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 27.06			82LK	T
	gl	25	0.5 ($NaClO_4$)	β_{122} 35.56			82LK	T

TABLE 53. 3,5-Dihydroxy-7-sulfo-2-naphthoic Acid $C_{11}H_8O_7S$

Metal	Method	t/°C	I_c/M	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	$\lg(K_3/M^{-1})$	Reference	Category
H^+	gl	25	0.5 ($NaClO_4$)	12.355	8.45	2.50	82LS	T
	sp	25	0.5 ($NaClO_4$)	12.374	8.37	2.52	82LS	T
Be^{2+}	gl	25	0.5 ($NaClO_4$)	13.64	7.149		82LS	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 20.004			82LS	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 29.848			82LS	T
	gl	25	0.5 ($NaClO_4$)	β_{122} 37.996			82LS	T
Al^{3+}	gl	25	0.5 ($NaClO_4$)	16.001	8.088	6.760	82LS	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 20.651			82LS	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 32.443			82LS	T

cont'd

TABLE 53. 3,5-Dihydroxy-7-sulfo-2-naphthoic Acid $C_{11}H_8O_7S$ (continued)

Cu^{2+}	gl	25	0.5 ($NaClO_4$)	10.205	5.68	82LS	T
	gl	25	0.5 ($NaClO_4$)	β_{111} 17.805		82LS	T
	gl	25	0.5 ($NaClO_4$)	β_{112} 24.60		82LS	T
	gl	25	0.5 ($NaClO_4$)	β_{122} 33.162		82LS	T

4. REFERENCES

51C Cochran, W. *Acta Cryst. 4* (1951) 376.

68M McBryde, W.A.E. *Can. J. Chem. 46* (1968) 2385.

70SS Sathe, R.M. and Shetty, S.Y. *J. Inorg. Nucl. Chem. 32* (1970) 1383.

71FS Fidelis, I. and Siekierski, S. *J. Inorg. Nucl. Chem. 33*(1971) 3191.

74HK Hague, D.N. and Kinley, K. *J.Chem.Soc., Dalton Trans.* (1974) 249.

74SRa Saarinen, H., Raikas, T. and Lajunen, L. *Finn. Chem. Lett.* (1974) 109.

74SRb Saarinen, H., Raikas, T. and Rauhala, A. *Finn. Chem. Lett.* (1974) 104.

75CE IUPAC Commission on Equilibrium Data, *Coord. Chem. Rev. 35B* (1975) 17.

75DI Dudeney, A.W.L. and Irving, R.J. *J.Chem.Soc., Faraday Trans. I 71* (1975) 1215.

75JK Jahagirda, D.V. and Khanolkar, D.D. *Indian J. Chem. 13* (1975) 168.

75L Lajunen, L.H.J. *Finn. Chem. Lett.* (1975) 1.

75LS Lowe, B.M. and Smith, D.G. *J.Chem.Soc., Faraday Trans. I 71* (1975) 1379.

75SG Scharff, J.P. and Genin, R. *Anal. Chim. Acta 78* (1975) 201.

76ABa Abbasi, S.A., Bhat, B.G. and Singh, R.S. *Inorg. Nucl. Chem. Lett. 12* (1976) 391.

76ABb Abbasi, S.A., Bhat, B.G. and Singh, R.S. *Indian J.Chem. 14A* (1976) 718.

76DV Dukanovic, A.B., Velasevic, K.R. and Cupic, Z.V. *Bull. Soc. Chim. Beograd 41* (1976) 41.

76KD Kul'ba, F.Ya., Drozhzhina, O.P. and Platunova, N.B. *Khim., Nauchn. Dokl. Gertsenovskie Chteniya, 28th* (1976) 4.

76La Lajunen, L.H.J. *Finn. Chem. Lett.* (1976) 36.

76Lb Lajunen, L.H.J. *Finn. Chem. Lett.* (1976) 63.

76Lc Lajunen, L.H.J. *Ann.Acad.Sci.Fenn. A 179* (1976) 62s.

76Ld Lee, Y-H. *Acta Chem. Scand. A30* (1976) 586.

76Le Lee, Y-H. *Acta Chem. Scand. A30* (1976) 593.

76ML Mäkitie, O., Lajunen, L.H.J. and Tamminen, P. *Finn.Chem.Lett.* (1976) 3.

76SJ Shelke, D.N. and Jahagirdar, D.V. *Bull.Chem.Soc.Jp. 49* (1976) 2142.

76SS Sandhu, S.S., Sandhu, R.S. and Kumaria, J.N. *Thermochim. Acta 15* (1976) 244.

77AR Aditya, S., Roy, A.K. and Lahiri, S.C. *Z. Phys. Chem. (Leipzig) 258* (1977) 1033.

77BB Burns, J.H. and Baldwin, W.H. *Inorg. Chem. 5* (1977) 289.

77DC Dwivedi, K., Chandra, M. and Dey, A.K. *Transition Met.Chem. 2* (1977) 186.

77DS Deshpande, R.G., Shelke, D.N. and Jahagirdar, D.V. *Indian J. Chem.15A* (1977) 320.

77FB Falicheva, A.I., Burdykina, R.I. and Shatalova,V.I.*Izv.Vyssh. Uchebn. Zaved., Khim.Khim.Tekhnol. 20* (1977) 166.

77GG Gladilovich, D.B., Grigor'ev, N.N. and Stolyarov, K.P. *Vestn. Leningr.Univ..Fiz., Khim.* (1977) 120.

77JK Jain, U., Kumari, V., Sharma, R.C., and Chaturvedi, G.K. *J.Chim.Phys. 74* (1977) 1038.

77KT Kostromina, N.A., Ternovaga, T.V., Shestakova, M.T. and Pirkes, S.B.*Koord. Khim. 3* (1977) 1008.

77MM Marigangaiah, Gowda, B.T. and Mahadevappa, D.S. *Current Science 46* (1977) 560.

77MS Martell, A.E. and Smith, R.M. *Critical Stability Constants, Vol. 3*, Plenum Press, New York, 1977.

77PS Perlmutter-Hayman, B., Secco, F., Tapuhi, E. and Venturini, M. *J. Chem. Soc., Dalton Trans.* (1977) 2220.

77PT Perlmutter-Hayman, B. and Tapuhi, E. *Inorg. Chem. 16* (1977) 2742.

77Q Queen, A. *Can. J. Chem. 55* (1977) 3035.

77SJ Shelke, D.N. and Jahagirdar, D.V. *J.Inorg.Nucl.Chem. 39* (1977) 2223.

77SK Sandhu, S.S., Kumaria, J.N. and Sandhu, R.S. *Thermochim. Acta 18* (1977) 329.

77TJ Taqui Khan, M.M. and Jyoti, M.S. *Indian J. Chem. 15A* (1977) 1002.

77UB Urbancik, L. and Bartusek, M. *Coll. Czech. Chem. Comm. 42* (1977) 446.

78AK Arena, G., Kavu, G. and Williams, D.R. *J.Inorg.Nucl.Chem. 40* (1978) 1221.

78AS Avdeef, A., Sofen, S.R., Bregante, T.L. and Raymond, K.N. *J. Am. Chem. Soc. 100* (1978), 5362.

78JS Jadhav, P.D., Shelke, D.N. and Bhobe, R.A. *J. Inorg. Nucl. Chem. 40* (1978) 572.

78La Lajunen, L.H.J. *Finn. Chem. Lett.* (1978) 127.

78Lb Lajunen, L.H.J. *Finn. Chem. Lett.* (1978) 129.

78LKa Lajunen, L.H.J. and Karvo, M. *Anal.Chim.Acta 97* (1978) 423.

78LKb Lajunen, L.H.J. and Karvo, M. *Acta Chem.Scand. A32* (1978) 370.

78LT Lajunen, L.H.J. and Tikanmäki, M. *Finn.Chem.Lett.* (1978) 96.

78MB Mikesova, M. and Bartusek, M. *Chem.zvesti 32* (1978) 472.

78RM Rajan, K.S., Mainer, S. and Davis, J.M. *J.Inorg.Nucl.Chem. 40* (1978) 2089.

78SDa Sharma, R.C., Dhindsa, S.S. and Bhargava, D.N. *Monatsh.Chem. 109* (1978)179.

78SDb Sharma, R.C., Dhindsa, S.S. and Bhargava, D.N. *Chem.Era* (1978) 443.

79A Abbasi, S.A. *Chem.Era 15* (1979) 8.

79CP Chouaib, F. and Poitrenaud, C. *Anal. Chim. Acta 108* (1979) 333.

79DD David, F. and David, P.G. *J. Coord. Chem. 9* (1979) 155.

79LE Lajunen, L.H.J., Eloranta, J. and Kukkohovi, A. *Finn.Chem.Lett.* (1979) 11.

79LKa Lajunen, L.H.J., Karvo, M. and Tikanmäki, M. *Finn.Chem.Lett.* (1979) 45.

79LKb Lajunen, L.H.J., Kostama, A. and Karvo, M. *Acta Chem.Scand. A33* (1979) 681.

79LP Lajunen, L.H.J., Parhi, S. and Ruotsalainen, H.*Finn.Chem.Lett.* (1979) 227.

79LS Lajunen, L.H.J. and Parhi, S. *Inorg. Nucl. Chem. Lett. 15* (1979) 311.

79LT Lajunen, L. and Tikanmäki, M. *Acta Univ.Oul. A74* (1979) 20 s.

79MB Mohan, M.S., Bancroft, D. and Abbott, E.H. *Inorg. Chem. 18* (1979)1527.

79NC Nair, G.M., Chander, K. and Joshi, J.K. *India, A.E.C., Bhabha At. Res. Cent. (Rep.)* 1979, B.A.R.C. -1005, 18.

79PT Perlmutter-Hayman, B. and Tapuhi, E. *Inorg. Chem. 18* (1979) 875.

79QD Queen, A., Davies, L. and Con, A. *Can. J. Chem. 57* (1979) 920.

79SJ Shelke, D.N. and Jahagirdar, D.V. *J.Inorg.Nucl.Chem. 41* (1979) 925.

79SV Singh, S.P., Verma, H.S. and Tandon, J.P. *J.Inorg.Nucl.Chem. 41* (1979) 587.

79VK Van den Berg, C.M.G. and Kramer, J.R. *Anal. Chim. Acta 106* (1979) 113.

80A Abbasi, S.A. *Pol.J.Chem. 54* (1980) 1377.

80CK Choi, S.U. and Kang, J.K. *Bull.Kor.Chem.Soc. 1* (1980) 105.

80JC Jagannadha Charyula, K., Chandra Pal, A.V. and Reddy, M.L.N. *Nat.Acad.Sci. Letters 3* (1980) 198.

80LH Lajunen, L.H.J. and Hiljanen, T. *Acta Univ.Oul. A105* (1980) 18s.

80LK Lajunen, L.H.J. and Karjalainen, J. *Kemia-Kemi 7* (1980) 614.

80LM Letkeman, P., Martell, A.E. and Motekaitis, R.J. *J.Coord.Chem. 10* (1980) 47.

80LP Lajunen, L.H.J., Petrola, R., Schildt, P., Korppi-Tommola, O. and Mäkitie, O.*Talanta 27* (1980) 75.

80LS Lajunen, L.H.J., Saarinen, J. and Parhi, S. *Talanta 27* (1980) 71.

80MS Mentasti, E., Secco, F. and Venturini, M. *Inorg. Chem. 19* (1980) 3528.

80NS Nemirovskii, V.D., Sokolova, I.V. and Raskin, M.N. *Khim. Drev.* (1980) 72.

80PS Perlmutter-Hayman, B., Secco, F., Tapuhi, E. and Venturini, M. *J.Chem.Soc., Dalton Trans.* (1980) 1124.

80YA Yousif, Y.Z. and Al-Imarah, F.J.M. *J.Inorg.Nucl.Chem. 42* (1980) 779.

81AS Abbasi, S.A. and Sharma, R.K. *J.Inorg.Nucl.Chem. 43* (1981) 625.

81C Chattopadhyaya, M.C. *J.Inst.Chemists (India) 53* (1981) 255.

81CPa Chitale, V.K. and Pitre, K.S. *J.Indian Chem.Soc. 58* (1981) 1207.

81CPb Chitale, V.K. and Pitre, K.S. *Nat.Acad.Sci.Letters 4* (1981) 247.

81CS Chattopadhyaya, M.C. and Singh, R.S. *J.Indian Chem.Soc. 58* (1981) 1203.

81EE El-Ezaby, M.S. and El-Khalafawy, T.E. *J.Inorg.Nucl.Chem. 43* (1981) 831.

81GS Gupta, V.P., Sthapak, J.K. and Sharma, D.D. *J.Inorg.Nucl.Chem. 43* (1981) 3019.

81LAa Lajunen, L.H.J., Aitta, E. and Parhi, S. *Talanta 28* (1981) 277.

81LAb Lajunen, L.H.J., Aitta, E. and Parhi, S. *Finn.Chem.Lett.* (1981) 65.

81LAc Lajunen, L.H.J., Anttila, R. and Hiljanen, T. *Oulun yliopiston Kemian laitoksen raporttisarja, Report no 1,* 1981.

81LL Lukkari, O. and Lukkari, H. *Finn. Chem. Lett.* (1981) 62.

81RM Rajan, K.S., Mainer, S., Rajan, N.L. and Davis, J.M. *J.Inorg. Biochemistry 14* (1981) 339.

81SY Singh, R.K.P., Yadava, P.C. and Yadava, K.L. *Nat.Acad.Sci.Letters 4* (1981) 437.

82AS Agarwal, R.C., Singh, H.N. and Saxena, R.C. *Thermochim. Acta 56* (1982) 371.

82C Chattopadhyaya, M.C. *J.Indian Chem.Soc. 59* (1982) 1416.

82CB Choppin, G.R., Bertrand, P.A., Hasegawa, Y. and Rizkalla, E.N. *Inorg. Chem. 21* (1982) 3722.

82CS Corigli, R., Secco, F. and Venturini, M. *Inorg. Chem. 21* (1982) 2992.

82DB Dubey, S.N. and Bhuyan, B.C. *Indian J.Chem. 21A* (1982) 442.

82DJ Dhat, C.R. and Jahagirdar, D.V. . *Indian J.Chem. Sect. A 21A* (1982) 792.

82EF Emara, M.M., Farid, N.A. and Wasfi, A.M. *Electrochim. Acta 27* (1982) 647.

82GS Gupta, V.P., Sthapak, J.K. and Sharma, D.D. *Indian J.Chem. 21A* (1982) 546.

82HN Hancock, R.D. and Nakani, B.S. *S. Afr. J. Chem. 35* (1982) 153.

82HO Hancock, R.A. and Orszulik, S.T. *Polyhedron 1* (1982) 313.

82LC Lal, U.S., Chattopadhyaya, M.C. and Dey, A.K. *J. Indian Chem. Soc. 59* (1982) 493.

82LK Lajunen, L.H.J. and Kopsa-Moilanen, V. *Finn.Chem.Lett.* (1982) 6.

82LS Lajunen, L.H.J., Seppänen, M., Nurmesniemi, H. and Leskelä, M. *Oulun Yliopiston Kemian Laitoksen Raporttisarja no. 8* (1982) 10s.

82MSa Mandlik, K.J., Saxena, C.P. and Khadikar, P.V. *Vijnana Parishad Anusandhan Patrika 25* (1982) 217.

82MSb Mentasti, E., Secco, F. and Venturini, M. *Inorg. Chem. 21* (1982) 602.

83A Abbasi, S.A. *Pol. J. Chem. 57* (1983) 727.

83B Bai, K.S. *Polyhedron 2* (1983) 513.

83IS Islam, M.M., Singh, R.S. and Bhat, B.G. *Transactions of the SAEST 18* (1983) 33.

83LE Lajunen, L.H.J., Eijärvi, E. and Häyrynen, H. *Acta Univ.Oul. A152* (1983)15s.

83LL Lajunen, L.H.J., Lippo, H., and Kokkonen, P. *Finn. Chem. Lett.* (1983)107.

83MS Mandlik, K.J., Saxena, C.P. and Khadikar, P.V. *J. Indian Chem. Soc. 60* (1983) 991.

83SG Sthapak, J.K., Gupta, V.P. and Sharma, D.D. *J.Indian Chem.Soc. 60* (1983) 705.

83ÖS Öhman, L. and Sjöberg, S. *Acta Chem. Scand. A37* (1983) 875.

84A Abbasi, S.A. *J.Indian Chem.Soc. 61* (1984) 125.

84CT Casassas, E. and Tauler, R. *J.Chim.Phys. 81* (1984) 233.

84HM Howlin, B., Mohd-Nor, A.R., Silver, J. and Barnard, P.W.C. *Inorg.Chim.Acta 91* (1984) 153.

84MA Marathe, D.G., Ambulkar, R.S. and Munshi, K.N. *Nat.Acad.Sci.Letters 7* (1984) 153.

84NH Nakani, B.S. and Hancock, R.D. *J. Coord. Chem. 13* (1984) 143.

84RR Reddy, P.R., Reddy, M.H. and Reddy, K.V. *Inorg. Chem. 23* (1984) 974.

84VS Venkatnarayana, G., Swamy, S.J. and Lingaiah, P. *Indian J. Chem. Sect. A 23A* (1984) 501.

85AS Anjaneyulu, Y., Swamy, R.Y. and Rao, R.P. *J.Indian Chem.Soc. 62* (1985) 346.

85CD Charlet, P., Deloume, J.P., Duc, G. and Thomas-David, G. *Bull.Soc. Chim.Fr.* (1985) 683.

85DD Daniele, P.G., De Robertis, A., De Stefano, C., Sammartano, S. and Rigano, C. *J. Chem. Soc., Dalton Trans.* (1985) 2353.

85IS Idriss, K.A., Seleim, M.M., Hassan, M.K., Abu-Bakr, M.S. and Sedaira, H. *Analyst 110* (1985) 705.

85KS Krishnamoorthy, C.R., Sunil, S. and Ramalingam, K. *Polyhedron 4* (1985)1451.

85LSa Limaye, S.N. and Saxena, M.C. *J.Indian Chem.Soc. 62* (1985) 572.

85PM Paal, T. and Mate, M. *Magy. Kem. Foly. 91* (1985) 569.

85SA Skorik, N.A. and Artish, A.S. *Zh. Neorg. Khim. 30* (1985) 1994.

85SB Shenyang, T. and Baoxin, Z. *Acta Scientiarum Naturalium* (1985) 27.

85VS Venkatnarayana, G., Swamy, S.J. and Lingaiah, P. *Indian J. Chem. Sect. A 24A* (1985) 624.

86AD Aplincourt, M., Debras-Bee, A., Gerard, C. and Hugel, R.P. *J.Chem.Res.(S)* (1986) 134.

86CL Choppin, G.R., Liu, Q. and Niu, C. *Lanthanide and Actinide Res. 1* (1986) 285.

86DV Diez-Caballero, R.J.B., Valentin, J.F.A., Garcia, A.A. and Batanero, P.S. *Bull. Soc. Chim. Fr.* (1986) 375.

86LL Lajunen, L.H.J., Lajunen, M. and Choppin, G.R. *Inorg.Chim.Acta 119* (1986) 87.

86LS Limaye, S.N. and Saxena, M.C. *Can. J. Chem. 64* (1986) 865.

86NS Narayana, G.V., Swamy, S.J. and Lingaiah, P. *Indian J. Chem. Sect. A 25A* (1986) 491.

86PS Petho, G. and Szász, G. *Magy. Kem. Foly. 92* (1986) 495.

87DS Diebler, H., Secco, F. and Venturini, M. *J.Phys.Chem. 91* (1987) 5106.

87GM Goncalves, M.L.S. and Mota, A.M. *Talanta 34* (1987) 839.

87GN Gerard, C., Njomgang, R., Pierrard, J-C., Rimbault, J. and Hugel, R.P. *J.Chem.Res.(S)* (1987) 294.

87MM Maeda, M., Murata, Y. and Kaname, I. *J. Chem. Soc., Dalton Trans.* (1987)1853.

87PB Pant, P.C., Bhatt, D.BP. and Chandra, M. *Chim. Acta Turc. 15* (1987) 223.

88DO Dahlund, M. and Olin, Å. *Acta Chem. Scand. A42* (1988) 273.

88LK Lajunen, L.H.J., Kokkonen, P. and Anttila, R. *Finn.Chem.Lett. 15* (1988) 101.

88LL Lajunen, L.H.J., Lajunen, M., Choppin, G.R. and Kemin Yao *Oulun Yiopiston Kemian laitoksen raporttisarja Report n:o 26* (1988) 31.

88LTb Lukkari, O. and Tamminen, J. *Finn. Chem. Lett. 15* (1988) 13.

88XJ Xu, J. and Jordan, R.B. *Inorg.Chem. 27* (1988) 1502.

89AP Aplincourt, M., Pierrard, J-C., Prudhomme, J-C. and Rimbault, J. *J.Chem.Res. (S)* (1989) 10.

89HM Hasegawa, Y., Morita, Y., Hase, M. and Nagata, M. *Bull. Chem. Soc.Jpn. 62* (1989) 1486.

89KKa Kiss, T., Kozlowski, H., Micera, G. and Erre, L.S. *Polyhedron 8* (1989) 647.

89KKb Kiss, T., Kozlowski, H., Micera, G. and Strinna Erre, L. *J.Coord.Chem. 20* (1989) 49.

89YA Yousif, Y.Z. and Al-Imarah, J.M. *Transition Met.Chem. 14* (1989) 123.

90DO Dahlund, M. and Olin, Å. *Acta Chem.Scand. 44* (1990) 321.

90JK Jezowska-Bojczuk, M., Kozlowski, H., Zubor, A., Kiss, T., Branca, M., Micera, G. and Dessi, A. *J.Chem.Soc., Dalton Trans.* (1990) 2903.

90RN Rizkalla, E.N., Nectoux, F., Dabos-Seignon, S. and Pagés, M. *Radiochim. Acta 51* (1990) 113.

90RP Ren, J.-M., Pei, F.-K. and Wang, W.-Y. *Chinese J. Chem.* (1990) 512.

91K Kiss, T., Sovago, I. and Gergely, A. *Pure & Appl. Chem. 64* (1991) 597.

92AL Anttila, R. and Lajunen, L.H.J. *Oulun Yliopiston kemian laitoksen raporttisarja, University of Oulu, Report no 37*, 1992.

92TI Tochiyama, O., Inoue, Y. and Narita, S. *Process. Metall.* 7A (Solvent Extr.1990, Pt. A) (1992) 669.

93AK Anttila, R., Kivimäki, A.-M., Lajunen, L.H.J., Laitinen, R.S. and Jokisaari, J. *Radiochim. Acta 61* (1993) 201.

93AL Anttila, R., Lajunen, L.H.J., Jokisaari, J. and Laitinen, R.S. *Acta Chem. Scand. 47* (1993) 535.

93KA Kiss, T., Atkari, K., Jezowska-Bojczuk, M. and Decock, P. *J. Coord. Chem. 29* (1993) 81.

93WW Wu, L. and Williams, D.R. *Chem. Speciation Bioavailability 5* (1993) 61.