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CRITICAL EVALUATION OF STABILITY CONSTANTS FOR α -HYDROXYCARBOXYLIC ACID COMPLEXES WITH PROTONS AND METAL IONS AND THE ACCOMPANYING ENTHALPY CHANGES** PART II. ALIPHATIC 2-HYDROXYCARBOXYLIC ACIDS***

(IUPAC Technical Report)

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Critical evaluation of stability constants for α -hydroxycarboxylic acid complexes with protons and metal ions and the accompanying enthalpy changes.

Part II. Aliphatic 2-hydroxycarboxylic acids

(IUPAC Technical Report)

Abstract: Stability constants for different aliphatic 2-hydroxycarboxylic acid complexes in aqueous solutions with protons and metal ions published between 1960 and the end of 1994 have been critically evaluated.

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1. INTRODUCTION

The hydroxy carboxylic acids and their derivatives are important chemicals in the pharmaceutical, biological, food, and general industrial chemical fields. The technological, practical, and industrial applications of these compounds have led to numerous studies of their properties and characteristics.

Various hydroxy acids occur naturally. They may contain an asymmetric carbon atom and are then potentially resolvable. The naturally occurring hydroxy acids are in general optically active. No stereoselectivity has been reported for any of these compounds.

The hydroxycarboxylic acids contain two donor groups, the hydroxyl and the carboxylate groups, and therefore they are all potentially bidentate ligands. The proton and metal ion complexation constants of these ligands strongly depends on the relative positions of the two donor groups in the molecule. Thus, the presence of the hydroxyl function in the 2-position to the carboxylic acid group results in an increased acidity of the latter. The effect on the dissociation behavior of the carboxyl group decreases rapidly with the distance between the two functions and becomes unimportant when acting through four or more atoms. Thus, the dissociation constants of 4-hydroxy acids do not differ substantially from those of the corresponding unsubstituted alkanolic acids. Also, the metal ion complexation with these ligands is strongly influenced by the relative position of the two groups. The 2-hydroxy acids form considerably stronger complexes with most metal ions, through bidentate chelation involving both functional groups, than do the corresponding simple carboxylic acids. Hydroxyl groups more distant from the carboxylic groups do not generally participate in the formation of chelate complexes, and the ligand coordination to metal ions occurs via the carboxyl group only.

The hydroxy carboxylic acids form stable complexes with most metal ions. Owing to the considerable number of reported data, in the form of protonation and metal ion binding constants, in this paper, the critical evaluation of the equilibrium data is restricted to proton and metal ion complexation with aliphatic monoprotic 2-hydroxy acids, in aqueous solution, published between 1960 and 1994. Only a few relevant data, published earlier, are included in this paper. Enthalpy changes, when available, are also reported. Equilibrium data obtained in nonaqueous or in solvent mixtures, as well as those dealing with the formation of mixed complexes, are not surveyed in this paper.

Many determinations of acid dissociation constants and metal ion complexation constants with hydroxy acids have been reported. Various experimental methods have been used for the measurements, mainly potentiometry, spectroscopy, and distribution between two phases. Several studies have been carried out in media of constant ionic strength (commonly in the range 0.1–2.0 mol dm⁻³), the supporting electrolytes being sodium perchlorate, but also sodium chloride, potassium chloride, and nitrate. The majority of the measurements has been performed at 25 °C.

1.1 Equilibrium constants

In this paper, the proton formation constants, K_{HL} , of hydroxycarboxylic acids are reported as protonation constants

$$K_{HL} = [\text{HL}]/[\text{H}^+][\text{L}^-] \quad (1)$$

For metal ion complexation, either the stepwise stability constants K_n ($n = 1, 2, 3, \dots, n$), defined as

$$K_n = [\text{ML}_n]/[\text{ML}_{n-1}][\text{L}] \quad (2)$$

or the overall stability constants, β_n ($n = 1, 2, 3, \dots, n$)

$$\beta_n = [\text{ML}_n]/[\text{M}][\text{L}]^n \quad (3)$$

are used (charges are omitted).

When protonated, hydroxo- or polynuclear species are formed. The overall stability constants, $\beta_{p,q,r}$ are used, where

$$\beta_{p,q,r} = [\text{M}_p\text{H}_q\text{L}_r]/[\text{M}]^p[\text{H}]^q[\text{L}]^r \quad (4)$$

Negative subscripts for H refer to proton removal from the complexes, according to the reaction:



1.2 Reported values

For accurate measurements of stability constants, particular care must be devoted to experimental details. Different experimental factors affect the stability constant values. These factors include appropriate choice of the experimental method employed for the measurements, the temperature control, correct choice and control of the ionic strength, correct calibration of the experimental apparatus used, accurate determination of concentration of the reagents, and method of data calculation (i.e., graphical, numerical, or computational methods).

The equilibrium data reported in the literature have, therefore, been evaluated according to the above-mentioned factors and grouped into three distinct categories, following the new suggestions of the IUPAC Commission on Equilibrium Data: recommended values (R) when the reported data are the results of at least two or more independent measurements, are consistent with other properties of the investigated system, and are in agreement with the data of similar systems (if they are available); provisional values (P) when only one value of stability constant, estimated accurate, is available and any additional values were obtained by the same research group; when insufficient or no experimental details are reported, the stability constant values cannot be accepted as accurate and, therefore, are rejected (Rj). Only recommended and provisional values are given in the tables of this report.

Once a number, two or more, of acceptable data were available, the stability constant values were averaged, and the final result is regarded as recommended if the standard deviation, $\sigma(\lg K)$, is less than 0.05 or regarded as provisional when $0.05 < \sigma(\lg K) < 0.2$. Enthalpy changes accompanying the proton and the metal ion complexation are frequently reported together with formation constant values. The enthalpy values can be obtained either by the temperature variation method, according to the van't Hoff equation

$$\partial(\ln K)/\partial T = \Delta H/RT^2 \quad (6)$$

or directly from calorimetric measurements. Even though the latter method gives generally more accurate values of the heats of formation of the complexes, the enthalpy changes calculated by temperature variation method are of similar precision provided that the stability constants are carefully measured at several different temperatures.

In this paper, the order of arrangement of the ligands is: 2 (α)-hydroxycarboxylic acids, substituted 2-hydroxycarboxylic acids. Within each class of ligands the order is by increasing ligand molecular weight.

The protonation constants and metal ion complex formation constants are reported in separated tables. Metal ions are arranged as follows: main group elements, transition metals, and f-block elements.

For each ligand, the order of the proton and metal ion formation constants is by (i) ionic strength (from zero ionic strength to the highest one), (ii) supporting electrolyte (NaClO_4 , KNO_3 , KCl , NaCl , NaNO_3), and (iii) year of reference.

Stability constants extrapolated to zero ionic strength are indicated by $\rightarrow 0$, those corrected to zero ionic strength using some theoretical or empirical formula are indicated by 0 corr.

1.3 Abbreviations

amp	amperometry
cal	calorimetry
Cat	evaluation category
CD	circular dichroism
con	conductivity
coul	coulometry
dis	distribution between two phases

ele	electrophoresis
esr	electron spin resonance
gl	potentiometry using glass electrode
H	potentiometry using hydrogen electrode
ix	ion exchange
kin	rate of reaction
M	potentiometry using metal electrode
M/Hg	potentiometry using amalgam electrode
NMR	nuclear magnetic resonance
pH	pH-metry, not specified
pol	polarography
qh	potentiometry using quinhydrone electrode
red	potentiometry using redox electrode
sol	solubility
sp	spectrophotometry
volt	voltammetry
T	temperature variation

2. PROTONATION CONSTANTS OF 2-HYDROXYCARBOXYLIC ACIDS

Aliphatic hydroxycarboxylic acids behave both as acids and alcohols. In many reactions, the two functions do not interfere with each other, especially if the two groups are far apart.

As mentioned above, the hydroxyl group has a marked influence on the dissociation behavior of the carboxyl group. The electron-withdrawing properties of the hydroxyl group induce an increase in acid strength of the carboxyl group. Typical of the inductive effects, they decrease rapidly with the distance between the two functions. Thus, the 2-hydroxyacetic acid is more than 10 times as strong as the acetic acid, 3-hydroxypropanoic acid is only twice as strong as propanoic acid, and 4-hydroxybutanoic acid is about as strong as butanoic acid.

The protonation constants reported in this paper are expressed as mixed (M) or concentration (C) constants, according to the electrode calibration method used. Mixed constants include both hydrogen ion activity and ligand concentration terms and are obtained when the electrode calibration is performed by using standard buffer solutions. Concentration constants include only concentration terms and are obtained by calibrating the electrodes with solutions of known hydrogen ion concentration.

Many determinations of protonation constants of 2-hydroxycarboxylic acids have been reported, especially for the first two members of the series, the glycolic and lactic acids. The majority of the measurements has been carried out potentiometrically, using glass electrodes, at 25 °C. The ionic strengths most used are 0.1 and 1.0 mol dm⁻³.

The literature values for the protonation constants of glycolic acid are collected in Table 1.

Table 1 Protonation constants of 2-hydroxyacetic acid (glycolic acid).

Method	Type of constant	I_c/M	$t/^\circ\text{C}$	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
H	C	$\rightarrow 0$	0.3	3.875		36N	R
H			12.5	3.844			R
H			25	3.831			R
H			37.5	3.833			R
H			50	3.849			R
qh	C	$\rightarrow 0$	25	3.83		53KE	R

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Table 1 (Continued).

Method	Type of constant	I_c/M	$t/^\circ\text{C}$	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
con	C	$\rightarrow 0$	25	3.83		75HV	R
con			30	3.83			R
con			35	3.83			R
gl	M	0.1 (NaClO ₄)	25	3.65		68ES	P
gl	M	0.1 (KNO ₃)	25	3.75	11.11	78JS	P
gl	C	0.1 (KNO ₃)	25	3.65		94PR	P
gl	M	0.1 (KCl)	30	3.70		62CT	P
gl	C	0.2 (NaClO ₄)	25	3.53		73SM	P
C			35	3.56			P
C			45	3.59			P
gl	C	0.2 (KCl)	25	3.58		93MS	P
gl	M	0.47 (NaClO ₄)	25	3.44		71RR	P
gl	C	0.5 (NaClO ₄)	25	3.61		68T	P
H	C	0.5 (NaClO ₄)	25	3.56		77CM	P
gl	M	0.5 (KNO ₃)	20	3.52		83BS	P
qh, gl	C	1.0 (NaClO ₄)	20	3.58		53A	R
qh	C	1.0 (NaClO ₄)	25	3.55		63LC	P
gl	C	1.0 (NaClO ₄)	25	3.62		63MP	R
gl	C	1.0 (NaClO ₄)	20	3.63		70PC	R
H	C	1.0 (NaClO ₄)	25	3.61		71BV	R
qh	C	1.0 (NaClO ₄)	20	3.62		73MB	R
gl	C	1.0 (NaClO ₄)	20	3.63		74K	R
gl	C	1.0 (NaClO ₄)	20	3.58		74MT	R
gl	C	1.0 (NaClO ₄)	25	3.61		76DB	R
gl	?	1.0 (NaClO ₄)	25	3.669		77BM	P
gl	C	1.0 (NaClO ₄)	25	3.60		79ZK	R
gl	C	1.0 (NaClO ₄)	25	3.60		81LL	R
gl	C	1.0 (NaClO ₄)	25	3.53		87ID	P
gl	C	2.0 (NaClO ₄)	0.5	3.72		72CD	P
			25	3.72			R
			52	3.72			P
gl	C	2.0 (NaClO ₄)	25	3.75		72DC	R
qh	C	2.0 (NaClO ₄)	25	3.77		73FP	R
gl	C	2.0 (NaClO ₄)	25	3.62		85AM	P
gl	C	3.0 (NaClO ₄)	25	3.923		77RW	P

The results at zero ionic strength [36N, 53KE, 75HV], obtained using different experimental techniques, are in excellent agreement with each other and are recommended. Several values have been reported at 0.1 mol dm⁻³ ionic strength. The result of 87AI is too low compared to those reported by other authors and is rejected. Too few experimental details are given in 62SB, and the corresponding value should be therefore rejected. The values of 75CSa seem to involve some error in the calculation of the protonation constants and are, therefore, to be considered at best as doubtful. Insufficient experimental details make the values reported by 77JK, 77RB, and 77RT doubtful, and thus they are not reported in this review. The data reported at 0.2 mol dm⁻³ ionic strength by 70RB and 76AM are rejected, the former because of the inaccuracy in making up the solutions used in the measurements, the latter because the protonation constant is too low. A great number of protonation constants has been reported at 1.0 mol dm⁻³ ionic strength. The majority of the results are in excellent agreement and are regarded as recommended or provisional. Other protonation constants evaluated as unreliable, and therefore re-

jected, are those of 69BB because they are too high and those of 74PS and 76SSa because they are too low. Good agreement is shown in the values reported in 72CD, 72DC, and 73FP at 2.0 mol dm⁻³ ionic strength, and they are recommended. The remaining values in Table 1 are regarded as provisional.

The reported protonation constants for lactic acid are listed in the Table 2. For this acid too, a great number of protonation constants have been reported at different temperatures and ionic strengths.

Table 2 Pronation constants of 2-hydroxypropanoic acid (lactic acid).

Method	Type of constant	I_c/M	$t/^\circ\text{C}$	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
con	C	$\rightarrow 0$	0	3.88		37MT	P
con	C		10	3.868			P
con	C		20	3.857			P
con	C		25	3.858			R
con	C		30	3.861			R
con	C		35	3.867			R
con	C		50	3.895			R
con	C	$\rightarrow 0$	25	3.86		75HV	R
con	C		30	3.86			R
con	C		35	3.86			R
gl	M	0.1 (NaClO ₄)	31	3.83		62CM	P
gl	M	0.1 (NaClO ₄)	25	3.77		69ES	P
gl	M	0.1 (KNO ₃)	25	3.74		67VA	R
gl	M	0.1 (KNO ₃)	25	3.69		74FP	R
gl	M	0.1 (KNO ₃)	25	3.69		88SK	R
gl	C	0.1 (KNO ₃)	25	3.64		94PR	R
gl	C	0.15 (NaClO ₄)	37	3.666		87BB	R
coul	C	0.15 (NaCl)	25	3.51		93GM	P
			37	3.70			R
gl	C	0.2 (NaClO ₄)	35	3.54	11.04	69RB	P
gl	C	0.2 (NaClO ₄)	45	3.53	10.95		P
gl	C	0.2 (NaClO ₄)	55	3.51	10.40		P
gl	C	0.2 (NaClO ₄)	25	3.57		73SM	R
	C		35	3.59			P
	C		45	3.61			P
gl	M	0.2 (NaClO ₄)	25	3.54		76AM	P
			35	3.48			P
			45	3.48			P
gl	C	0.2 (NaClO ₄)	30	3.53	10.90	88J	P
gl	C	0.2 (KCl)	25	3.58		93MS	R
gl	C	0.2 (KCl)	25	3.52		94KS	R
gl	M	0.47 (NaClO ₄)	25	3.50		71RR	P
gl	C	0.5 (NaCl)	25	3.50		70AB	P
gl	C	0.6 (NaCl)	25	3.572		86MS	P
gl	C	1.0 (NaClO ₄)	20	3.626		65JL	R
gl	C	1.0 (NaClO ₄)	25	3.64		65TV	R
qh	C	1.0 (NaClO ₄)	25	3.65		65VT	R
gl	C	1.0 (NaClO ₄)	25	3.63		71Bva	R
qh	C	1.0 (NaClO ₄)	20	3.64		73MB	R
gl	C	1.0 (NaClO ₄)	20	3.65		74MT	R
gl	?	1.0 (NaClO ₄)	25	3.656		77BM	R
dis	C	1.0 (NaClO ₄)	25	3.63		84LL	R

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Table 2 (Continued).

Method	Type of constant	I_c/M	$t/^\circ\text{C}$	$\lg(K_1/M^{-1})$	$\lg(K_2/M^{-1})$	Reference	Category
gl	C	1.0 (NaClO ₄)	25	3.63		87ID	R
gl	C	2.0 (NaClO ₄)	25	3.80		72DC	R
qh	C	2.0 (NaClO ₄)	25	3.82		73FP	R
gl	C	2.0 (NaClO ₄)	25	3.79		76KG	R

The zero ionic strength values [37MT, 75HV] are in excellent agreement with each other and are recommended. At higher ionic strengths, good agreement is shown in the constants measured at 0.2 and 1.0 mol dm⁻³, respectively. Most of the data are reliable and the protonation constants appear accurately determined. Accordingly the corresponding values are recommended or provisional. In a few cases, the experimental details were insufficient or too few and/or the protonation constants too high or too low as compared with the majority of the reported values, probably because of some error in the measurements or in the calculation of the constants. These values were considered to be rejected [62SB, 67ES, 68BV, 68T, 71AL, 71H, 71M, 73LS, 77RT, 80J, 93GL].

For glycolic and lactic acids, the huge number of published data makes it possible to select recommended values of their protonation constants in a rather wide range of ionic strength. The corresponding values are collected in the Table 3.

Table 3 Recommended values for the protonation constants of glycolic and lactic acids.

Ligand	$t/^\circ\text{C}$	I_c/M	Type of constant	$\lg(K_1/M^{-1})$
Glycolic acid	25	0.0	C	3.83
	25	1.0	C	3.61
	25	2.0	C	3.75
Lactic acid	25	0.0	C	3.86
	37	0.15	C	3.68
	25	1.0	C	3.64
	25	2.0	C	3.80

For other 2-hydroxy acids (2-hydroxybutanoic acid, 2-hydroxypentanoic acid, and 2-hydroxyhexanoic acid), only a few protonation constant values are available. The literature data for these acids are collected in Table 4. The reported values are acceptable and are regarded as provisional.

The loss of a proton from the hydroxyl group has been reported only for glycolic and lactic acids. The deprotonation of the hydroxyl group is displayed at very high pH values where the pH measurements with glass electrodes are of low accuracy. The corresponding values have been rejected.

The data reported in Tables 1–4 show that, as expected, the protonation constants of these ligands are close to each other and that the length of the aliphatic chain has only a small influence on the basicity of the ligands.

A comparison of the mixed protonation constant values with those of concentration constants, obtained under the same experimental conditions, shows that they differ by about ≈ 0.1 logarithmic units.

Table 4 Protonation constants of 2-hydroxybutanoic acid, 2-hydroxypentanoic acid, and 2-hydroxyhexanoic acid.

Method	Type of constant	I_c/M	$t/^\circ\text{C}$	$\lg(K_1/M^{-1})$	Reference	Category
2-Hydroxybutanoic acid						
con	C	$\rightarrow 0$	25	3.84	75HV	P
			30	3.86	75HV	P
			35	3.86	75HV	P
gl	M	0.1 (NaClO ₄)	31	3.81	62CM	P
gl	M	0.1 (NaClO ₄)	25	3.695	69ES	P
gl	C	0.2 (KCl)	25	3.76	93MS	P
qh	C	2.0 (NaClO ₄)	25	3.80	73FP	P
qh	C	2.0 (NaClO ₄)	25	3.80	74GM	P
2-Hydroxypentanoic acid						
con	C	$\rightarrow 0$	25	3.79	75HV	P
			30	3.80		P
			35	3.81		P
gl	M	0.1 (NaClO ₄)	25	3.75	69ES	P
gl	C	1.0 (NaClO ₄)	25	3.59	68GG	P
2-Hydroxyhexanoic acid						
con	C	$\rightarrow 0$	25	3.90	75HV	P
			30	3.91		P
			35	3.91		P
gl	M	0.1 (NaClO ₄)	25	3.68	69ES	P

3. STABILITY CONSTANTS OF METAL COMPLEXES WITH 2-HYDROXYCARBOXYLIC ACIDS

Many determinations of metal ion complexation constants with acids of this series have been published. The majority of the investigations has been devoted to studies of metal complex formation of glycolic and lactic acids. In some cases [77RW and 77RWa], the metal ion-induced deprotonation of the alcoholic-OH groups and its subsequent coordination also occurs at various pH values. The deprotonation of the alcoholic groups occurs at high pH values.

Various experimental methods have been used to determine the complex formation constants. Potentiometry was the most used method, but spectrophotometry, polarography, and distribution between two phases have also been used.

The formation constants of metal ion complexes with glycolic and lactic acids are listed in Tables 5 and 6, respectively. The equilibrium data for the other 2-hydroxycarboxylic acids have been collected in Table 7.

3.1 Formation constants of complexes of 2-hydroxyacetic acid (glycolic acid)

For most of the main group elements, single values of stability constants have been reported (see Table 5). Data are available for all alkaline earth metal ions. The complexation of Be²⁺ has been studied by the ion-exchange method [65BK]. The measurements were performed at a pH value too high to exclude the hydrolysis of the ion. The reported stability constant is consequently too high and is rejected. The remaining values for other alkaline earth metal ions should be considered as provisional.

Table 5 Stability constants of metal complexes of 2-hydroxyacetic acid (glycolic acid).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
Mg ²⁺	H	0.0	25	1.33				54DM	P
	H	0.2 (KCl)	25	0.92				38CK	P
Ca ²⁺	sol	0.0	25	1.59				38D	P
	sol	0.0	25	1.65				75DN	P
			30	1.75					P
			35	1.84					P
			40	1.95					P
			45	2.02					P
Sr ²⁺	H	0.2 (KCl)	25	1.11				38CK	P
	sol	0.0	25	1.31				52CM	P
	H	0.2 (KCl)	25	0.80				38CK	P
Ba ²⁺	sol	0.0	25	1.04				52CM	P
	H	0.0	25	0.98				54DM	P
	H	0.2 (KCl)	25	0.66				38CK	P
B(III)	gl	0.21 (KNO ₃)	21	$\lg K[\text{B}(\text{OH})_3 + \text{L}^- = \text{B}(\text{OH})_2\text{H}_1\text{L}^- + \text{H}_2\text{O}]$				77RB	P
				0.17 (pH < 7)					
				0.54 (pH > 7)					
Ga ³⁺	gl	0.2 (NaClO ₄)	25	3.39	6.53	9.20		76AM	P
			35	3.42	6.59	9.44			P
			45	3.45	6.65	9.63			P
In ³⁺	gl	0.14 (HClO ₄)	25	2.95				60WT	P
	gl	0.2 (NaClO ₄)	25	2.91	5.44			73SM	P
			35	3.00	5.58				P
			45	3.07	5.70				P
	dis	0.3 (HClO ₄)	25	3.15				60WT	P
	dis	0.5 (NaClO ₄)	25	2.95	5.45			68T	P
	gl	2.0 (NaClO ₄)	20	2.93	5.52	7.31	7.98	53S	P
Pb ²⁺	pol	1.0 (NaClO ₄)	30	1.90	3.16			66JG	P
	gl, Pb/Hg	1.0 (NaClO ₄)	25	2.01	2.94			71BV	P
	pol	2.0 (NaClO ₄)	25	1.90	3.04	3.38		70FB	P
	qh	2.0 (NaClO ₄)	25	1.83	2.86	3.15 D	4.28	70FM	P
VO ²⁺	gl	1.0 (NaClO ₄)	25	2.56	4.22	5.19		81LL	P
	gl	0.2 (KCl)	25	2.66(2)	4.39(2)			93MS	P
				$\lg K[\text{VO}^{2+} + \text{L}^- = \text{VOH}_1\text{L} + \text{H}^+] = -1.35$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_1\text{L}_2^- + \text{H}^+] = 0.89$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_2\text{L}_2 + 2\text{H}^+] = -3.98$					P
				$\lg K[\text{VOH}_1\text{L} + \text{L}^- = \text{VOH}_1\text{L}_2^-] = 2.24$					P
Mn ²⁺	con	0.0	25	1.582				54EM	P
Fe ²⁺	gl	1.0 (NaClO ₄)	25	1.33				73BL	P
Fe ³⁺	gl, red	1.0 (NaClO ₄)	25	2.90				73BL	P
	gl, red	1.0 (NaClO ₄)	25	$\lg K[\text{Fe}^{3+} + \text{L}^- = (\text{FeH}_1\text{L})^+ + \text{H}^+] = 1.59$				73BL	P
				$\lg K[\text{Fe}^{3+} + 2\text{L}^- = (\text{FeH}_1\text{L}_2) + \text{H}^+] = 4.00$					P
				$\lg K[\text{Fe}^{3+} + 3\text{L}^- = (\text{FeH}_1\text{L}_3)^- + \text{H}^+] = 5.50$					P
	gl, red	1.0 (NaClO ₄)	20	2.5				74K	P
Co ²⁺	con	0.0	25	1.975				54EM	P
	ix	0 corr	25	1.96	3.01			65SM	P
	ix	0.05 (NaClO ₄)	25	1.76				58SL	P
	ix	0.16 (NaClO ₄)	25	1.64				57LW	P
	ix	0.16 (NaClO ₄)	25	1.60				58SL	P
	ix	0.23 (NaClO ₄)	25	1.51				58SL	P
Ni ²⁺	con	0.0	25	2.261				54EM	P
	con	0 corr	20	2.32				83IS	P
	gl	1.0 (NaNO ₃)	30	2.17	3.77			69BB	P

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Table 5 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
Cu ²⁺	sol	0.0	25	2.89	4.66			54EM	P
	sol	0.0	25	3.10				75DN	P
			30	3.16					P
			35	3.22					P
			40	3.32					P
			45	3.37					P
	ix	0.1 – 1.0	20		$\lg K_2 = 1.42$	$\lg K_3 = 0.3$		64L	P
	gl	1.0 (NaClO ₄)	25	2.36	3.70			63MP	P
	gl,Cu/Hg	1.0 (NaClO ₄)	25	2.27	3.74			72BV	P
	pol	2.0 (NaClO ₄)	25	2.40	3.65	3.90	4.18	70FB	P
	sp	2.0 (NaClO ₄)	25	2.46				76GF	P
Zn ²⁺	Cu/Hg	3.0 (NaClO ₄)	25	2.39	3.11	4.31		69W	P
	ix	0.16 (NaClO ₄)	25	1.89					P
	H	0.2 (KCl)	25	1.92				38CK	P
	ix	0.23 (NaClO ₄)	25	1.81					P
	ix	0.5 (NaClO ₄)	23	1.78	2.70			80PS	P
	dis	0.75 (NaClO ₄)	25	1.86	3.11			69L	P
	qh	1.0 (NaClO ₄)	25	1.92	2.93	3.00	4.04	63LC	P
	dis	1.0 (NaClO ₄)	23	1.85	3.32	3.80		78PS	P
	qh	2.0 (NaClO ₄)	25	1.72	2.88	3.00		70FM	P
	Zn/Hg	3.0 (NaClO ₄)	25	1.79	2.61	3.27		69W	P
	Zr ⁴⁺	kin	0 corr	25	$\lg K[\text{Zr}(\text{OH})_2^{2+} + \text{L}^- = \text{Zr}(\text{OH})_2\text{L}^+] = 7.70$				73KP
con		0.0	25	1.866				54EM	P
Cd ²⁺	pol	1.0 (NaClO ₄)	30	1.26	2.15			66JG	P
	gl, Cd/Hg	1.0 (NaClO ₄)	25	1.22	2.08			75BJ	P
	qh	2.0 (NaClO ₄)	25	1.51	1.84			70FM	P
	Cd/Hg	3.0 (NaClO ₄)	25	1.68	2.74	3.37		69W	P
Hf ⁴⁺	kin	0 corr	25	$\lg K[\text{Hf}(\text{OH})_2^{2+} + \text{L}^- = \text{Hf}(\text{OH})_2\text{L}^+] = 7.30$				73KP	P
	WO ₄ ²⁻	nmr	21	$\lg K[\text{WO}_4^{2-} + 2\text{L}^- + 2\text{H}^+ = \text{WO}_2\text{H}_2\text{L}_2^{2-} + 2\text{H}_2\text{O}] = 15.7$				87CR	P
Hg ₂ ²⁺	gl	3.0 (NaClO ₄)	25	3.01	5.71			77RWa	P
Hg ²⁺	gl	3.0 (NaClO ₄)	25	3.60	7.05			77RW	P
Sc ³⁺	gl	0.1 (KNO ₃)	25	4.40				84II	P
Y ³⁺	qh	2.0 (NaClO ₄)	20	2.47	4.40	5.70	6.26	60S	P
	qh	2.0 (NaClO ₄)	25	2.38	4.35	5.61		61CC	P
Ce ³⁺	qh	2.0 (NaClO ₄)	20	2.35	4.02	5.15	5.54	59S	R
	qh	2.0 (NaClO ₄)	25	2.27	4.01	5.12		61CC	R
Ce ⁴⁺	kin	1.5 [(H ⁺ ,Na ⁺)ClO ₄] pH < 0.5		$\lg K[\text{Ce}^{4+} + \text{HL} = \text{Ce}(\text{HL})^{4+}]$					
			11.4	1.45				77AM	P
			17.6	1.29					P
			25	1.30					P
			30	1.42					P
					$\lg K[\text{CeOH}^{3+} + \text{HL} = \text{CeL}^{3+} + \text{H}_2\text{O}]$				
Ce ⁴⁺			11.4	2.56					P
			17.6	2.30					P
			25	2.08					P
			30	1.76					P
	sp	1.5 [(H ⁺ ,Na ⁺)ClO ₄] pH < 0.5		$\lg K[\text{Ce}^{4+} + \text{HL} = \text{Ce}(\text{HL})^{4+}]$					
			11.4	1.52					P
		17.6	1.40					P	
		25	1.34					P	
		30	1.36					P	

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Table 5 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category	
Dy ³⁺	qh	2.0 (NaClO ₄)	20	2.52	4.48	5.90	6.48	59S	R	
	qh	2.0 (NaClO ₄)	25	2.48	4.45	5.60		66CF	R	
Er ³⁺	gl	0.5 (NaClO ₄)	25	2.62	4.67	6.10		77CM	P	
	qh	2.0 (NaClO ₄)	20	2.60	4.58	5.99	6.48	59S	R	
	qh	2.0 (NaClO ₄)	25	2.64	4.53			66CF	R	
Eu ³⁺	sp	2.0 (NaClO ₄)	21	2.58	4.62	5.87	6.63	81BMa	R	
	dis	0 corr	25	2.52				72CD	R	
	dis	0.08 (NaClO ₄)	25	2.69				62MM	R	
	qh	0.5 (NaClO ₄)	20	2.57	4.61	5.91	6.36	62G	R	
	qh	2.0 (NaClO ₄)	25	2.45	4.41	5.77		61CC	R	
	dis	2.0 (NaClO ₄)	0.5	2.55	4.56			72CD	R	
				10	2.54	4.54				R
				25	2.52	4.58				R
Gd ³⁺	qh	0.2 (NaClO ₄)	20	2.73	4.79	6.30	7.11	61S	P	
	gl	0.5 (NaClO ₄)	25	2.53	4.61	5.82	7.15	77CM	P	
	ix	1.0 (NaClO ₄)	20	2.54	4.48	5.85		59Sa	P	
	qh	2.0 (NaClO ₄)	20	2.48	4.43	5.79	6.42	59S	R	
	qh	2.0 (NaClO ₄)	25	2.46	4.33	5.89		61CC	R	
	qh	3.0 (NaClO ₄)	20	2.59	4.60	6.11	6.81	61S	P	
	qh	2.0 (NaClO ₄)	20	2.54	4.48	5.91	6.43	59S	R	
	qh	2.0 (NaClO ₄)	25	2.49	4.53	5.91		61CC	R	
Ho ³⁺	gl	2.0 (NaClO ₄)	25	2.46	4.42	5.68		62BC	R	
	sp	2.0 (NaClO ₄)	21	2.50	4.60	5.81	6.63	81BMa	R	
	gl	0.5 (NaClO ₄)	25	2.28	3.86	5.19		77CM	P	
La ³⁺	qh	2.0 (NaClO ₄)	20	2.19	3.76	4.81	5.08	59S	R	
	qh	2.0 (NaClO ₄)	25	2.14	3.94			66CF	R	
La ³⁺	gl	2.0 (NaClO ₄)	25	2.14	3.79	4.90	5.92	85AM	P	
	qh	2.0 (NaClO ₄)	25	2.67	4.76			66CF	R	
Lu ³⁺	qh	2.0 (NaClO ₄)	20	2.51	4.34	5.57	6.04	59S	R	
	sp	2.0 (NaClO ₄)	20	2.54	4.40	5.30		59S	R	
	qh	2.0 (NaClO ₄)	25	2.41	4.38	5.33		66CF	R	
Nd ³⁺	sp	2.0 (NaClO ₄)	21	2.41	4.38	5.33	6.25	81BM	P	
	gl	0.5 (NaClO ₄)	25	2.49	4.37	5.51		77CM	P	
	qh	2.0 (NaClO ₄)	20	2.43	4.19	5.40	5.95	59S	R	
Pr ³⁺	gl	0.5 (NaClO ₄)	25	2.54	4.59	5.69	7.20	77CM	P	
	qh	2.0 (NaClO ₄)	20	2.56	4.53	5.86	6.45	59S	R	
	qh	2.0 (NaClO ₄)	25	2.46	4.40	5.86		61CC	R	
Tb ³⁺	qh	2.0 (NaClO ₄)	25	2.40	4.45			66CF	R	
	qh	2.0 (NaClO ₄)	25	2.63	4.66	6.12		66CF	R	
Tm ³⁺	qh	2.0 (NaClO ₄)	25	2.63	4.66	6.12		66CF	R	
	gl	0.5 (NaClO ₄)	25	2.72	4.97			77CM	P	
Yb ³⁺	qh	2.0 (NaClO ₄)	20	2.72	4.82	6.32	6.78	59S	R	
	qh	2.0 (NaClO ₄)	25	2.62	4.82	6.22		61CC	R	
	qh	2.0 (NaClO ₄)	25	2.62	4.82	6.22		61CC	R	
Th ⁴⁺	qh	1.0 (NaClO ₄)	20	3.98	7.36	9.95	11.95	73MB	P	
	gl, qh	1.0 (NaClO ₄)	25	4.11	7.45	10.18	11.97	78DR	P	
UO ₂ ²⁺	gl	0.1 (KCl)	30	2.97	5.37			62CTa	P	
	gl	0.1 (NaClO ₄)	31	2.93	5.15			76SS	P	
	ix	0.16 (NaCl)	25	2.78	4.08			57LW	P	
	qh, gl	1.0 (NaClO ₄)	20	2.42	3.96	5.20		53A	R	
	gl	1.0 (NaClO ₄)	20	2.38	3.95	5.18		74MT	R	
	gl	1.0 (NaClO ₄)	25	2.35	3.98	5.17		76DB	R	
NpO ₂	sp	0.1 (NaClO ₄)	25	1.51				69ES	P	
	dis	1.0 (NaClO ₄)	25	1.21	1.70			83IT	P	

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Table 5 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
NpO_2^+	dis	1.0 (NaClO_4)	25	1.31	2.06			92TI	P
NpO_2^{2+}	gl	1.0 (NaClO_4)	20	2.37	3.95	5.00		72PT	P
PuO_2^{2+}	sp	0.1 (NaClO_4)	25	2.43	3.79			68ES	P
	gl	1.0 (NaClO_4)	20	2.16	3.45	4.27		70PC	P
	gl	1.0 (NaClO_4)	20	2.16	3.45	4.25		74MT	P
Am^{3+}	ix	0.5 (NaClO_4)	20	2.82	4.86	6.30		62G	P
	dis	2.0 (NaClO_4)	0.5	2.66	4.46			72CD	P
			10	2.61	4.46				P
			25	2.59	4.40				P
			53	2.49	4.47				P
Cm^{3+}	ix	0.5 (NaClO_4)	20	2.84	4.75			63G	P
	dis	2.0 (NaClO_4)	0.5	2.63	4.46			72CD	P
			25	2.59	4.56				P
			41	2.52	4.40				P
			52	2.52	4.34				P
Bk^{3+}	dis	2.0 (NaClO_4)	0.5	2.73	4.64			72CD	P
			10	2.70	4.64				P
			25	2.65	4.70				P
			41	2.62	4.52				P
			53	2.57	4.55				P
Cf^{3+}	dis	2.0 (NaClO_4)	53	2.63	4.60			72CD	P

Several data are available concerning the complexes of indium(III). Taking in due consideration the slightly different ionic strengths used, the values of 60WT and 73SM are in fairly good agreement with that of 68T, obtained by solvent extraction method. These values are regarded as provisional. The remaining values have been rejected because of insufficient experimental details [74PS, 75CS] or because they seem to be too high [76SSa]. The potentiometric data of 53S at 2.0 mol dm⁻³ ionic strength are accurately determined and are therefore provisional.

The potentiometric value of 70RB for the Tl^{1+} complex and 75CS for the Tl^{3+} complex appear too high and are rejected, the amperometric values of 80IA for the Tl^{3+} complexes appear unreliable and are rejected because the authors report different formation constant values at slightly different pH values.

A few data are available for the lead(II) complexes. The polarographic value of 66JG is in fairly good agreement with the potentiometric value of 71BV, which appears to be determined accurately. These values are provisional. At higher ionic strength (2.0 mol dm⁻³), the values of 70FB and 70FM are also in good agreement but are from the same research group and are provisional. The stability constants determined at 3.0 mol dm⁻³ ionic strength are somewhat high and are rejected [65BWa]. Reports on the complexes of transition-metal ions are numerous. According to the mentioned criteria, the data have been rejected when the accuracy of the measurements was not known or the experimental conditions were not clearly specified. This is the case for the data concerning the complexes of iron(III) [72NB, 76SC], zirconium(IV) [70KK], and hafnium(IV) [81HL].

Several papers have been published on the complexation of the divalent transition elements cobalt, nickel, copper, zinc, and cadmium.

The majority of the data on the cobalt(II) complexes have been obtained by the ion-exchange method. The values of 57LW and 58SL are from the same group and are provisional. The zero ionic strength values [54EM, 65SM] are in excellent agreement and are provisional. The stability constant of 80PS appears to be too low compared with the values reported by other authors and is rejected. The last two values at 2.0 mol dm⁻³ ionic strength are from the same group and are rejected, the potentiometric one [70FM] because, as the authors admit, an interaction occurs between quinhydrone and the metal

ion, the spectrophotometric one [70GF] because the temperature of the experiments is not well specified.

Also for the nickel(II) complexes, no recommended values can be given. The zero ionic strength values of 70RB and 88J are unreliable because they are too high. The stability constants of 54EM and 83IS are in good agreement with each other and are provisional. Insufficient experimental details make the value of 74HO doubtful. The values of 69BB are accurately determined and are, therefore, provisional, while those of 70FM and 70GF are doubtful for the same reasons given above for the complexes of cobalt(II).

As for the copper(II) complexes, independent measurements [63MP, 72BV] report stability constant values of K_1 , which are in good agreement with each other and are, therefore, provisional. The values of 70SG are considered as doubtful because the experimental conditions are not well specified. The values at 2.0 mol dm^{-3} ionic strength are from the same research group and are regarded as provisional [70FB, 76GF] or doubtful (70GF) because of the uncertainty in the temperature used in the measurements. The remaining values are provisional.

Several papers report the formation constants of Zn^{2+} complexes. Two papers [73SS, 77S], from the same group, report the formation constants for four successive mononuclear complexes. The stability constants were obtained by an indirect polarographic method, using cadmium(II) [73SS] and indium(III) [77S] as the indicator ions. The reported values are too low and, despite the different ionic strengths used (0.5 and 1.0 mol dm^{-3} , respectively) they are exactly the same. These values are rejected. Independent measurements at 1.0 mol dm^{-3} ionic strength [63LC, 78PS] are in good agreement and are provisional. From the same research group, the values of 70FB and 70FM are calculated at $I = 2.0 \text{ mol dm}^{-3}$. The polarographic values [70FB] are regarded as doubtful because of the large error introduced in the graphical calculation of the formation constants, whereas the potentiometric values, which appear more accurately determined, are provisional. The remaining values are regarded as provisional or rejected according to the adopted criteria [54EM, 58SL, 70FB, 77S].

Only a few reports are available for the cadmium(II) complexes. Due to good agreement, the values at $I = 1.0 \text{ mol dm}^{-3}$ are provisional. The polarographic value of 70FB must be rejected for the same reasons mentioned above for the zinc(II) complexes. The remaining values are reliable and, therefore, provisional [54EM, 70FM, 69W].

Equilibrium data concerning the complexation of mercury(I) and mercury(II) [77RW, 77RWa] are from the same group. From a comparison of the formation constants of these ions with acetate and glycolate, the authors conclude that unchelated complexes are formed in both cases.

The remaining values are all regarded as provisional.

The glycolic acid and, in general, all the 2-hydroxycarboxylic acids have received particular and continued attention for their applicability as eluents in cation-exchange processes. In particular, the complexes of the trivalent rare earths with these acids exhibit a more or less regularly increasing stability with increasing atomic number, which makes these ligands particularly valuable and useful in the separation of rare earth mixtures by ion-exchange techniques. As a consequence, many determinations of complexation constants of these ions with glycolate, as well as with other 2-hydroxy acids have been reported.

The values of 80PP are questionable and therefore rejected, first because the experimental conditions are not clearly specified and secondly because of the unjustified assumptions in the treatment of the experimental data. Also rejected are the stability constants reported in 86LS: the values are too high, likely because possible hydrolytic processes, which would yield higher values of the complex formation constants, have not been taken into account. The ion-exchange values of 83J are rejected because they are too low. In good agreement, in spite of the slightly different temperatures used for the measurements, the very accurately determined values of 59S, 61CC, and 66CF are recommended. The ion-exchange values of 60SV cannot be accepted because the reported stability constants of the cerium(III) complexes with this ligand are exactly the same, including the standard deviations, as those obtained

for the complexes with lactate and 2-hydroxyisobutyrate. In addition, the values reported in 62CT, 68L, 76BM, and 77BMA cannot be accepted.

Among the actinide elements, the uranyl(VI) complexes are the most studied. The potentiometric values of 62CTa and 76SS are in excellent agreement and can be regarded as provisional. The polarographic and potentiometric values of 87ID are unreliable because they are too high. The values obtained by solvent extraction are doubtful, and are thus rejected in this review [62SB]. The values of 53A, 74MT, and 76DB show excellent agreement and are recommended. The remaining values are provisional.

The available data for the Th^{4+} complexes are from the same research group and are provisional, as well as those for the neptunium(VI) and plutonium(VI) complexes.

The neptunium(V) complexes have been studied by several authors. The ion-exchange values of 65MM are rejected because the background electrolyte is unknown and because the stability constants have been determined in a ligand concentration range too high for the method used. The value of 82IT cannot be accepted because the experimental conditions are not well specified. The value of 90RN seems to be too high and is rejected. The remaining values seem to be accurately determined and are provisional.

The ion-exchange values of 71MO for the Pu^{3+} complexes are rejected because the experimental conditions are not clearly specified.

As for the transplutonium elements, equilibrium data are available for the trivalent ions americium, berkelium, californium, and curium. Generally, these elements are not available in amounts suitable for conventional chemical investigations, and, therefore, the data concerning these elements have been obtained by ion exchange or distribution between two liquid phases. The reported constants have been evaluated as provisional.

3.2 Formation constants of complexes of 2-hydroxypropanoic acid (lactic acid)

A large number of stability constants of metal ion complexes with lactate has been reported (Table 6).

The alkaline earth metal ions all form rather weak complexes with lactate, which makes it considerably difficult to obtain reliable values of stability constants. As a consequence, most of the data reported in Table 6 have been rejected [65BK, 70GN, 73LD, 75TD, 93GM].

Table 6 Stability constants of metal complexes of 2-hydroxypropanoic acid (lactic acid).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
Mg^{2+}	gl	0.15 (NaClO_4)	37	1.235				87BB	P
	H	0.2 (KCl)	25	0.93				38CK	P
	qh	1.0 (NaClO_4)	25	0.73	1.30			65VT	P
	ix	1.0 (NaClO_4)	25	0.75	1.27			73LD	P
Ca^{2+}	sol	0.0	25	1.47				38D	P
	H	0.2 (KCl)	25	1.07				38CK	P
	sol	0.2–0.8 (NaL)	25	1.23				79KB	P
	gl,Ca	0.5 (NaCl)	25	0.92	1.62			81MV	P
	qh	1.0 (NaClO_4)	25	0.90	1.24			65VT	P
	ix	1.0 (NaClO_4)	25	0.91	1.45			73LD	P
Sr^{2+}	sol	0.0	25	0.96				52CM	P
	H	0.2 (KCl)	25	0.70				38CK	P
	qh	1.0 (NaClO_4)	25	0.53	0.69			65VT	P
	ix	1.0 (NaClO_4)	25	0.61	0.95			73LD	P
Ba^{2+}	sol	0.0	25	0.77				52CM	P
	H	0.2 (KCl)	25	0.55				38CK	P
	qh	1.0 (NaClO_4)	25	0.34	0.42			65VT	P

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Table 6 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category		
B(III)	gl	0.1 (KNO ₃)	25					84PS	P		
									P		
									P		
								70LN			
									P		
									P		
Al ³⁺	gl	0.2 (KCl)	25					94KS	P		
									P		
									P		
									P		
									P		
									P		
	ele, gl	0.2 (NaNO ₃)	20	2.38	4.56	6.66			71H	P	
		0.6 (NaCl)	25	2.36	4.42	5.79			86MS	P	
	gl, nmr	0.6 (NaCl)	25						90MO	P	
										P	
										P	
	gl	1.0 (ClO ₄ ⁻)	25	2.26	4.88				75TD	P	
			35	2.28	4.94					P	
			45	2.40	5.26					P	
		25	2.26					85TD	P		
		25	2.25					85TD	P		
		25	3.28	6.37	9.29			76AM	P		
Ga ³⁺	gl		35	3.41	6.56	9.50			P		
			45	3.51	6.77	9.74			P		
			25	3.14	5.74				73SM	P	
In ³⁺	gl	0.2 (NaClO ₄)	35	3.21	5.87				P		
			45	3.29	6.00				P		
			25	2.96	5.62				68T	P	
	Pb ²⁺	dis	0.5 (NaClO ₄)	25	2.96	5.62				68T	P
				25	3.26	6.07	7.47	8.5		72SSa	P
				25	1.98	2.98				67TG	R
		qh	1.0 (NaClO ₄)	25	1.99	2.78				71BVa	R
				25	2.00	3.18				73LD	R
				25	2.12					85TD	P
		pol	1.0 (ClO ₄ ⁻)	25	2.16					85TD	P
				25	2.15	3.15	3.26	2.95		68FP	P
				25	2.16	3.23	3.67			76KG	P
				25	2.15	3.06	3.34			80TG	P
				3.5	2.115	3.06	3.34				P
				15.5	2.086	3.05	3.34				P
25	2.052			3.04	3.26				P		
34.5	2.037			3.06	3.24				P		
25	2.05			3.06				82TG	P		
sol	3.0 (NaClO ₄)	25	2.29	3.62				65BW	P		
		25	2.26	3.30	3.33			65BWa	P		
		25	2.26	3.30	3.33			65BWa	P		
VO ²⁺	gl	0.2 (KCl)	25	2.79	5.15				93MS	P	
										P	
										P	
										P	
										P	
										P	
	sp, CD	1.0 (NaClO ₄)	20							P	
											P
											P
											P
											P
											P

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Table 6 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category	
Cr ³⁺	gl	1.0 (ClO ₄ ⁻)	25	3.30	5.70	8.40		75TD	P	
	ix	1.0 (ClO ₄ ⁻)	25	3.18	5.70	8.28		75TD	P	
			35	3.65	6.36	8.04			P	
			45	3.08	5.18	8.00			P	
Mn ²⁺	qh	1.0 (NaClO ₄)	25	0.92	1.46	~1.56		67TG	P	
	ix	1.0 (NaClO ₄)	25	1.04	1.77			73LD	P	
Fe ³⁺	kin	1.0 (NaClO ₄)	25	$\lg K[\text{Fe}^{3+} + \text{HL} = \text{FeH}_{-1}\text{L} + 2\text{H}^+] = -1.59$				79M	P	
Co ²⁺	qh	1.0 (NaClO ₄)	25	1.37	2.32	~2.52		67TG	P	
			ix	1.0 (NaClO ₄)	25	1.40	2.56		73LD	P
	gl	1.0 (NaClO ₄)	25	1.36	2.30	2.89		73WK	P	
	sp	1.0 (NaClO ₄)	25	1.49	2.49			73WK	P	
	CD	2.0 (NaClO ₄)	20	1.38	2.30	2.30		72LN	P	
	gl	2.0 (NaClO ₄)	20	1.39	2.36	2.74		72LN	P	
	sp	2.0 (NaClO ₄)	25	1.28	2.53			72SS	P	
	qh	2.0 (NaClO ₄)	25	1.48	2.42	2.71		76KG	P	
	Ni ²⁺	kin	0	10	2.20				73HT	P
				20	2.20					P
25				2.18					P	
30				2.18					P	
con		0 corr	20	2.19				83IS	P	
qh		1.0 (NaClO ₄)	25	1.59	2.67	~2.97		67TG	R	
ix		1.0 (NaClO ₄)	25	1.65	3.08			73LD	R	
gl		1.0 (NaClO ₄)	25	1.69	2.85	3.24		73WK	R	
sp		1.0 (NaClO ₄)	25	1.76	2.90			73WK	P	
pol		1.0 (ClO ₄ ⁻)	25	1.77				85TD	P	
sol		1.0 (ClO ₄ ⁻)	25	1.74					P	
sp		2.0 (NaClO ₄)	25	1.57	2.94			72SS	P	
qh		2.0 (NaClO ₄)	25	1.71	2.84	3.50		76KG	P	
Cu ²⁺		sp	0.1 (NaClO ₄)	30	2.01	2.68			68RS	P
				gl	0.1 (KCl)	25	1.93	3.27		70GN
	35			2.06		2.70			P	
	sol	0.1 (KCl)	45	2.35	2.70				P	
			25	2.36	3.90			P		
			30	2.46	3.52			P		
			35	2.54	3.44			P		
			40	2.66	3.27			P		
			45	2.77	3.08			P		
			qh	1.0 (NaClO ₄)	25	2.49	3.98	~4.28		67TG
	gl	1.0 (NaClO ₄)	25	2.40	4.16	5.03		73WK	P	
	sp	1.0 (NaClO ₄)	25	2.40	4.29			73WK	P	
	gl, Cu/Hg	1.0 (NaClO ₄)	25	2.54	4.00			75BJ	P	
	pol	1.0 (ClO ₄ ⁻)	25	2.47				85TD	P	
	pol	2.0 (NaClO ₄)	25	2.52	4.04	4.46	4.18	65SF	P	
pol	2.0 (NaClO ₄)	25	2.54	4.11	4.48	4.18	68FP	P		
sp	2.0 (NaClO ₄)	25	2.63	4.10	5.27		72SS	P		
qh	2.0 (NaClO ₄)	25	2.66	4.28	4.89		76KG	P		
gl	2.0 (NaClO ₄)	20	2.57	4.69			80J	P		
sp	2.0 (NaClO ₄)	20	2.64	4.79			80J	P		
Zn ²⁺	H	0.2 (KCl)	25	1.86				38CK	P	
	qh	1.0 (NaClO ₄)	25	1.61	2.85	~3.15		67TG	P	
	ix	1.0 (NaClO ₄)	25	1.56	3.04			73LD	P	
	gl	1.0 (NaClO ₄)	25	1.43	2.43	3.11		73WK	P	
	qh	2.0 (NaClO ₄)	25	1.67	2.65	2.94		76KG	P	

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Table 6 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
MoO ₄ ²⁻				$\lg K[\text{MoO}_4^{2-} + 2\text{L}^- + 2\text{H}^+ = \text{MoO}_2\text{H}_{-2}\text{L}_2 + 2\text{H}_2\text{O}] = 14.7$				87CR	P
Pd ²⁺	gl	0.1 (KNO ₃)	25	2.02				88SK	P
Ag ⁺	ix	1.0 (NaClO ₄)	25	0.46	0.23			73LD	P
Cd ²⁺	qh	1.0 (NaClO ₄)	25	1.21	2.08	~2.28		67TG	P
	ix	1.0 (NaClO ₄)	25	1.30	2.37			73LD	P
	gl	1.0 (NaClO ₄)	25	1.38	2.29			73WK	P
	gl, Cd/Hg	1.0 (NaClO ₄)	25	1.24	1.88			75BJ	P
	pol	1.0 (ClO ₄ ⁻)	25	1.29				85TD	P
	sol	1.0 (ClO ₄ ⁻)	25	1.35				85TD	P
	pol	2.0 (NaClO ₄)	25	1.32	2.04	2.45	1.85	68FP	P
	qh	2.0 (NaClO ₄)	25	1.29	2.00	2.64		76KG	P
Y ³⁺	qh	2.0 (NaClO ₄)	25	2.53	4.70	6.12		61CC	P
Ce ³⁺	qh	2.0 (NaClO ₄)	25	2.33	4.10	5.21		61CC	P
	sp	1.5 (HClO ₄ + NaClO ₄)	10	1.49				77AM	P
			20	1.40					P
			25	1.18					P
			30	1.32					P
Ce ⁴⁺	kin	1.5 [(H ⁺ , Na ⁺)ClO ₄] pH < 0.5		$\lg K[\text{Ce}^{4+} + \text{HL} = \text{Ce}(\text{HL})^{4+}]$				77AM	
			10	1.52					P
			20	1.24					P
			25	1.18					P
			30	1.27					P
				$\lg K[\text{CeOH}^{3+} + \text{HL} = \text{CeL}^{3+} + \text{H}_2\text{O}]$					
			10	2.75					P
			20	2.39					P
			25	2.28					P
			30	2.05					P
	sp	1.5 [(H ⁺ , Na ⁺)ClO ₄] pH < 0.5		$\lg K[\text{Ce}^{4+} + \text{HL} = \text{Ce}(\text{HL})^{4+}]$					
			10	1.49					P
			20	1.40					P
			25	1.18					P
			30	1.32					P
Dy ³⁺	gl	0.1 (NaClO ₄)	25	3.09	5.38	5.95		66GG	P
	qh	2.0 (NaClO ₄)	25	2.72	4.77	6.77		66CF	P
Er ³⁺	gl	0.1 (NaClO ₄)	25	3.21	5.57	7.18		66GG	P
	qh	2.0 (NaClO ₄)	25	2.77	5.11	6.70		61CC	P
Eu ³⁺	dis	1.0 (NaClO ₄)	25	2.46	4.28	5.87	6.5	84LL	P
	qh	2.0 (NaClO ₄)	25	2.53	4.60	5.88		61CC	P
	dis	2.0 (NaClO ₄)	25	2.48	4.56	5.82		71AL	P
Gd ³⁺	gl	0.1 (NaClO ₄)	25	2.96	5.09			66GG	P
	qh	2.0 (NaClO ₄)	25	2.53	4.63	5.91		61CC	P
Ho ³⁺	qh	2.0 (NaClO ₄)	25	2.71	4.97	6.55		61CC	P
La ³⁺	gl	0.1 (NaClO ₄)	25	2.44	4.32			66GG	P
	qh	2.0 (NaClO ₄)	25	2.27	3.95	5.06		66CF	P
Lu ³⁺	gl	0.1 (NaClO ₄)	25	3.40	5.82	7.88		66GG	P
Nd ³⁺	pH, CD	0.5 (NaClO ₄)	25	2.595	4.36	6.09		81JP	P
	qh	2.0 (NaClO ₄)	25	2.47	4.37	5.60		61CC	P
	sp	2.0 (NaClO ₄)	21	2.45	4.39	5.44	6.25	81BMa	P
Pm ³⁺	ix, pH	0.2 (NaClO ₄)	20	2.43	4.20	5.35		68WZ	P
	ele	1.5 (KCl)	10	2.54	4.24			72SN	P

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Table 6 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
Pr^{3+}	gl	0.1 (NaClO_4)	25	2.69	4.96			66GG	P
	ix, pH	0.2 (NaClO_4)	20	2.46	4.27	5.62		68WZ	P
	pH, CD	0.5 (NaClO_4)	25	2.55	4.23	5.71		81JP	P
Sm^{3+}	pH, CD	0.5 (NaClO_4)	25	2.63	4.66	5.82		81JP	P
	qh	2.0 (NaClO_4)	25	2.56	4.58	5.90		61CC	P
Tb^{3+}	gl	0.2 (NaClO_4)	25	2.65	4.82	5.89	6.33	64DV	P
Yb^{3+}	qh	2.0 (NaClO_4)	25	2.85	5.27	6.96		61CC	P
Th^{4+}	gl	0.1 (NaClO_4)	20	4.16				85SA	P
	qh	1.0 (NaClO_4)	20	4.21	7.78	10.54	12.90	73MB	P
U^{4+}	gl	1.0 (NaClO_4)	25	4.40	8.3	11.8	15.1	84LL	P
				(lg $\beta_5 = 17.5$, lg $\beta_6 = 19.0$)					
UO_2^{2+}	dis	0.1 (NaClO_4)	20	2.81	4.56	5.46		62SB	P
	qh	1.0 (NaClO_4)	25	2.76	4.43	5.77		67TG	P
	gl	1.0 (NaClO_4)	20	2.77	4.52	5.78		74MT	P
	gl	1.0 (NaClO_4)	25	2.68	4.47	5.64		84LL	P
	pol	1.0 (ClO_4^-)	25	2.66				85TD	P
NpO_2^{2+}	sp	0.1 (NaClO_4)	25	1.75				69ES	P
	dis	1.0 (NaClO_4)	25	1.40	2.01			92TI	P
Am^{3+}	dis	1.0 (NaClO_4)	25	2.43	4.23	5.65	6.0	84LL	P
	ele	1.5 (KCl)	10	2.57	4.21			72SN	P
	dis	2.0 (NaClO_4)	25	2.52	4.77	5.98		71ALa	P
Cm^{3+}	ele	1.5 (KCl)	10	2.59	4.29			72SN	P

The ion-exchange values of 65BK and 73LD for the beryllium(II) complexes were determined at pH values too high to exclude the hydrolysis of the metal ion and are therefore rejected. Equilibrium data for biological conditions (37 °C and 0.15 mol dm⁻³ ionic strength) are available for magnesium(II) and calcium(II) [87BB, 93GM]. The value of 87BB appears accurately determined and is regarded as provisional. Those of 93GM are regarded very doubtful because they appear too low. Good agreement is shown in the values of the stability constants determined with different methods by 65VT, 73LD, and 81MV, and they are provisional.

The lactate complexes of aluminum(III), indium(III), and lead(II) are the most studied of the main group elements. For the Al³⁺ complexes, several data are available at different temperatures and ionic strengths. The values of 71H, 86MS, and 94 KS have been accurately determined, are in good agreement with each other, and are provisional. The values at $I = 1.0$ mol dm⁻³ are from the same research group, show good agreement, and are also provisional. The experimental conditions are not specified in 69PK and 72PK, and these values are rejected.

The indium(III) complexes have also been studied by different experimental methods. The values at $I = 0.1$ mol dm⁻³ are rejected because they are too low [75KK] or because of insufficient experimental data reported [75CS]. The remaining values are provisional.

Several data are available on the formation of complexes with lead(II). Excellent agreement is shown in the data at $I = 1.0$ mol dm⁻³ [67TG, 71BVa, 73LD], and they are recommended or provisional. Several data are available at $I = 2.0$ mol dm⁻³: they are all from the same research group and are provisional or rejected because they are too low [65SF] or too high [55MA]. Also, the values of 65BW, obtained by two different techniques, are provisional. Only isolated values of stability constants have been reported for the complexation of gallium(III), thallium(I), germanium(IV), tin(II), and antimony(III). The few reported data do not permit their classification, and these values have been rejected when the experimental conditions were not well specified [85SA, 69RB, 71WC, 75BP, 75W].

Many data are available on the complexation of transition-metal ions with lactate. Among them, the complexes of divalent cations cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) have been

studied by several authors, using different experimental methods, mostly potentiometry and polargraphy.

The values reported by 84MP and 80CKa are rejected either because the experimental conditions are not well specified or because the assumptions made by the authors appear arbitrary and unreliable, or both. Circular dichroism has been used to study the complexes of cobalt(II), nickel(II), and copper(II) at different ionic strengths [68BV], but the values of the stability constants are approximate and are therefore rejected. The formation constants for the nickel(II) complexes of 69RB and 88J are also rejected, because they are unusually high, and those of 93GL are rejected because of lack of experimental details. The polarographic value of 73SS for the zinc(II) complexes appears too low compared to the values reported by other authors and are rejected, too. Several values of formation constants for the complexes of these ions with lactate have been reported at $I = 1.0 \text{ mol dm}^{-3}$ [67TG, 73LD, 73WK, 85TD]. The reported values are in general in fairly good agreement, except those of 85TD for the cobalt(II) and zinc(II) complexes, which are lower and higher respectively than those reported in other papers. The very accurately determined copper(II) and cadmium(II) stability constants of 75BJ are provisional. Fairly good agreement is also shown in the data reported at $I = 2.0 \text{ mol dm}^{-3}$. The reported data at this ionic strength appear accurately determined and are all provisional.

As can be seen in Table 6, the copper(II) ion forms the most stable complexes of these ions, in agreement with the order of stability of Irving and Williams.

For the other transition-metal ions, only few data are available, and in many cases only single values of stability constants have been reported. In most cases, the experimental conditions are not specified, and the corresponding stability constants are thus rejected. This is the case for the complexation of Ti^{4+} [71ZP], Fe^{2+} [84GC], Fe^{3+} [84GC, 70PK, 76SC], Zr^{4+} [60RE, 64RM], and Hf^{4+} [60RE, 64RM, 81HL].

Two papers report data on the complexation of VO^{2+} with lactic acid [65JL, 93MS]. In both papers, the formation of mononuclear chelate complexes, ML and ML_2 , are reported, and the values of the complex formation constants are in very good agreement, taking into consideration the slightly different experimental conditions. In the more detailed work of 93MS, the species formed at higher pH values are also taken into consideration.

Very few data are reported for the manganese(II) complexes [67TG, 73LD, 57LW]. This ion forms rather weak complexes with lactate. The potentiometric value of 67TG is in good agreement with that obtained by ion-exchange method by 73LD, and these values are provisional, whereas the few experimental details and the relatively high pH used in 57LW requires that the reported stability constants be rejected.

For the remaining transition-metal ions, only isolated values of stability constants have been reported. The evaluation is, therefore, rather difficult, and in most cases the data are regarded as rejected [65DS, 68BV, 69RB, 70SG, 72AD, 78PS, 84MP, 85TD].

Several data have been reported on the complexation of lanthanide (including Sc^{3+} and Y^{3+}) and actinide elements.

As for the lanthanides, the general trend is, as for the glycolate complexes, a more or less regular increase of the stability constants of the complexes with increasing atomic number and, for each ion, a decrease in the stabilities of the complexes as the ionic strength increases.

The values of 73LS and 86LS are abnormally high because the authors do not take into account the hydrolysis of the ions and are rejected. The ion-exchange values of 60SV are rejected for the reasons mentioned above (see glycolate complexes). The results of 64DV appear too low, taking into consideration the ionic strength employed, and are rejected. The value reported for yttrium seems to be too high, and it is thus rejected [58PM]. The experimental conditions reported for promethium are insufficient to be accepted [67DV]. The values reported for holmium do not meet the requirements and are thus rejected [81BM].

The remaining values should be regarded as provisional.

Also, the complexes of the actinide elements have been studied by several authors. Among the tetravalent ions, data are available for thorium, uranium, and plutonium.

The potentiometric values of 73LS for the thorium(IV) complexes are rejected because they are too high and those of 85TD because they are too low. Good agreement is shown in the two remaining values, which are provisional.

Only one report deals with the uranium(IV) complexes [84LL]. The investigation was carried out very accurately, and the values are provisional. As the experimental conditions are not specified, the β_4 value reported by 66N for the Pu(IV) complex is rejected.

The uranium(VI) complexes have been studied by several authors. The stability constants reported by 62CM and 87ID, though accurately determined and obtained in a pH range where the hydrolysis of the metal cation can be excluded, are too high and are rejected. The values of 67MN and 67VA are too low and are rejected. Excellent agreement show the remaining values obtained at $I = 1.0 \text{ mol dm}^{-3}$, which are provisional.

For the neptunium(V) complexes, the ion-exchange values of 65MM are rejected because the experimental conditions are not well specified. The spectrophotometric value of 69ES is provisional. The remaining values are from the same research group and are rejected [82IT, 83IT] because the stability constants appear to be too low. The last value [92TI] is certainly more accurate and is provisional.

The experimental conditions for the determination of the stability constants of the plutonium(III) complexes are not clearly specified, and the reported data are rejected [71M].

As for the transplutonium elements, very few data are available. The value of 67ES for americium(III), curium(III), californium(III), and fermium(III) complexes are rejected. The remaining values 84LL, 72SN, and 71ALa for the americium(III) complexes and that of 72SN for the curium(III) complexes are provisional.

3.3 Formation constants of complexes of 2-hydroxybutanoic, 2-hydroxypentanoic, and 2-hydroxyhexanoic acids

These acids have not received the same attention as the glycolic and lactic acids. As a consequence, a rather small number of stability constants of metal complexes of these acids has been reported in the literature. The available data are collected in Table 7.

Table 7 Stability constants of metal complexes of 2-hydroxybutanoic acid, 2-hydroxypentanoic acid, and 2-hydroxyhexanoic acid.

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
2-Hydroxybutanoic acid									
Pb^{2+}	pol	2.0 (NaClO ₄)	25	2.10	2.78	3.57		73NP	P
	pol	2.0 (NaClO ₄)	25	2.10	2.75	3.58		73PG	P
	qh	2.0 (NaClO ₄)	25	2.16	3.32	4.03		78MM	P
	Pb/Hg	3.0 (NaClO ₄)	25	2.04	2.88	2.71		66WB	P
VO^{2+}	gl	0.2 (KCl)	25	3.10	5.89			93MS	P
				$\lg K[\text{VO}^{2+} + \text{L}^- = \text{VOH}_{-1}\text{L} + \text{H}^+] = -1.03(2)$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_{-1}\text{L}_2^- + \text{H}^+] = 1.64(4)$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_{-2}\text{L}_2 + 2\text{H}^+] = -3.03(1)$					P
				$\lg K[\text{VOH}_{-1}\text{L} + \text{L}^- = \text{VOH}_{-1}\text{L}_2^-] = 2.67$					P
Co^{2+}	sp	2.0 (NaClO ₄)	25	1.43	1.83			74GM	P
	qh	2.0 (NaClO ₄)	25	1.49	2.38	3.04		78MM	P
Ni^{2+}	sp	2.0 (NaClO ₄)	25	1.72	2.91	3.35		73GP	P
	sp	2.0 (NaClO ₄)	25	1.72	2.91	3.35		74GM	P
	qh	2.0 (NaClO ₄)	25	1.72	2.89	3.63		78MM	P

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Table 7 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
Cu^{2+}	sp	2.0 (NaClO_4)	25	2.67	4.71			74GM	P
	pol	2.0 (NaClO_4)	25	2.68	4.45	4.57	4.89	75FP	P
	qh	2.0 (NaClO_4)	25	2.63	4.31			75GM	P
Zn^{2+}	qh	2.0 (NaClO_4)	25	1.72	3.02	3.84	4.24	73FP	P
2-Hydroxybutanoic acid									
Cd^{2+}	pol	2.0 (NaClO_4)	25	1.23	2.13	2.25	2.45	73NP	P
	qh	2.0 (NaClO_4)	25	1.29	2.07	3.00		78MM	P
NpO_2^+	sp	0.1 (NaClO_4)	25	1.62				69ES	P
	dis	1.0 (NaClO_4)	25	1.64	2.13			92TI	P
2-Hydroxypentanoic acid									
Y^{3+}	gl	1.0 (NaClO_4)	25	2.46				68GG	P
Dy^{3+}	gl	1.0 (NaClO_4)	25	2.63				68GG	P
Er^{3+}	gl	1.0 (NaClO_4)	25	2.68				68GG	P
Eu^{3+}	gl	1.0 (NaClO_4)	25	2.43				68GG	P
Gd^{3+}	gl	1.0 (NaClO_4)	25	2.45				68GG	P
Ho^{3+}	gl	1.0 (NaClO_4)	25	2.64				68GG	P
La^{3+}	gl	1.0 (NaClO_4)	25	1.98				68GG	P
Lu^{3+}	gl	1.0 (NaClO_4)	25	2.76				68GG	P
Nd^{3+}	gl	1.0 (NaClO_4)	25	2.31				68GG	P
Pr^{3+}	gl	1.0 (NaClO_4)	25	2.24				68GG	P
Sm^{3+}	gl	1.0 (NaClO_4)	25	2.40				68GG	P
Tb^{3+}	gl	1.0 (NaClO_4)	25	2.53				68GG	P
Yb^{3+}	gl	1.0 (NaClO_4)	25	2.76				68GG	P
NpO_2^+	sp	0.1 (NaClO_4)	25	1.59				69ES	P
2-Hydroxyhexanoic acid									
NpO_2^+	sp	0.1 (NaClO_4)	25	1.63				69ES	P

For 2-hydroxybutanoic acid only the complexes of lead(II), among the main group elements, have been studied. For this system, the values of 73NP, 73PG, and 78MM are in excellent agreement, but, being from the same research group, are only provisional. The values of β_2 and β_3 appear to be too low and are rejected. Provisional too are the potentiometric values of 66WB, except for the value of β_3 , which is too low.

Equilibrium data are available for the transition-metal ions Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} . The data reported for these systems are from the same group: the stability constants appear accurately determined and are provisional. For the remaining transition-metal ion complexes, the formation constant of the iron(III) complex [76SC] is rejected because the hydrolysis of the ion cannot be excluded, whereas the potentiometric values of 93MS for the vanadyl(IV) complexes are provisional.

Among the f-block elements, data have been reported for the complexes of uranium(VI) and neptunium(V). Only one paper reports equilibrium data for the uranyl(VI) ion [62CM]. In this case too, as for the analogous complexes with lactate, the formation constants appear to be too high and are rejected. The stability constant values for the neptunium(V) complexes are reported in four papers, three of them from the same research group [82IT, 83IT, 92TI]. The values of 82IT and 83IT are too low and must be rejected. Those of 92TI, as well as those of 69ES, are acceptable and are regarded as provisional.

The only data available in the literature on the metal complexes of 2-hydroxypentanoic acid are those for the lanthanides(III) (Y^{3+} included) and neptunium(V). For the lanthanide(III) complexes, isolated values of stability constants are available for all the ions, Pm^{3+} excluded [68GG]. The lack of duplicate results makes evaluation difficult. The accuracy of the potentiometric measurements appears

good, and the reported values are provisional. Also provisional is the single value [69ES] reported for the neptunium(V) complex.

There is very little to be said about the metal complexes of 2-hydroxyhexanoic acid. The only formation constant value found in the literature deals with the complexation of neptunium(V) [69ES]. As for the values with other 2-hydroxy acids, this value is regarded as provisional.

4. SUBSTITUTED 2-HYDROXYCARBOXYLIC ACIDS

The protonation constants and the stability constants of metal ion complexes with substituted 2-hydroxycarboxylic acids reported in the literature are collected in Tables 8 and 9, respectively.

4.1 2-Hydroxy-2-methylpropanoic acid (α -hydroxyisobutyric acid)

4.1.1 Protonation constants

Most of the reported data are to be regarded as provisional.

The potentiometric value of 63DV, at zero ionic strength, is well supported by that of 75HV obtained by conductometric measurements. Insufficient experimental details are given in 71M (the temperature of the measurements is unknown), and the reported value is rejected. The potentiometric values of 62SB, and 66LN and 67LN appear to be too high and too low respectively, compared to those of other authors, and are also rejected.

No protonation enthalpy values for this ligand are available.

Table 8 Protonation constants of substituted 2-hydroxycarboxylic acids.

Method	Type of constant	I_c/M	$t/^\circ\text{C}$	$\lg(K_1/M^{-1})$	Reference	Category
2-Hydroxy-2-methylpropanoic acid (α -hydroxyisobutanoic acid)						
gl	M	0	25	4.00	63DV	P
con	C	0	25	4.00	75HV	P
	C		30	4.00		P
	C		35	4.00		P
gl	C	0.1 (NaClO ₄)	25	3.78	70CB	P
gl	M	0.1 (KNO ₃)	25	3.80	74PK	P
gl	M	0.2 (NaClO ₄)	25	3.792	63DV	P
gl	C	0.2 (KCl)	25	3.76(1)	93MS	P
gl	C	0.5 (NaClO ₄)	25	3.75	64SP	P
gl	C	0.5 (NaClO ₄)	25	3.75	79DT	P
qh	C	1.0 (NaClO ₄)	20	3.78	73MB	P
gl	C	1.0 (NaClO ₄)	20	3.79	74MT	P
gl	C	2.0 (NaClO ₄)	20	3.70	80J	P
2-Hydroxy-2-methylbutanoic acid						
gl	C	0.1 (KNO ₃)	25	3.73	69PC	P
gl	C	0.2 (KCl)		3.70	93MS	P
2-Hydroxy-3-methylbutanoic acid						
con	C	0	25	3.87	75HV	P
	C		30	3.88		
	C		35	3.89		

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Table 8 (Continued).

Method	Type of constant	I_c/M	$t/^\circ\text{C}$	$\lg(K_1/M^{-1})$	Reference	Category
2-Ethyl-2-hydroxybutanoic acid						
qh	C	1.0 (NaClO ₄)	25	3.64	65TV	P
gl	C	0.2 (KCl)	25	3.58	93MS	P
2-Hydroxy-2,3-dimethylbutanoic acid						
gh	C	1.0 (NaClO ₄)	25	3.80	65TV	P
2-Ethyl-2-hydroxy-3-methylbutanoic acid						
gl	C	0.1 (NaClO ₄)	25	3.59	76SP	P
2-Hydroxy-2,4-dimethylpentanoic acid						
qh	C	1.0 (NaClO ₄)	25	3.80	65TV	P
2-Hydroxy-2-propylpentanoic acid						
qh	C	1.0 (NaClO ₄)	25	3.80	65TV	P
2-Hydroxy-2-phenylacetic acid (mandelic acid)						
con	C	0 corr	25	3.41	38BD	P
gl	M	0 corr	25	3.39	78KK	P
gl	C	0.1 (NaClO ₄)	25	3.18	89HM	R
gl	M	0.1 (KNO ₃)	25	3.19	67PN	R
gl	C	0.1 (KNO ₃)	25	3.22	80BP	R
2-Hydroxy-2-phenylacetic acid (mandelic acid)						
	C	0.2 (KCl)	25	3.18	93MS	P
gl	C	0.5 (NaClO ₄)	25	3.27	70T	P
gl	C	0.5 (KNO ₃)	25	3.35	81CK	P
qh	C	1.0 (NaClO ₄)	25	3.16	66TV	P
qh	C	1.0 (NaClO ₄)	20	3.18	73MB	P
gl	C	1.0 (NaClO ₄)	20	3.21	74MT	P
gl	C	1.0 (NaClO ₄)	25	3.17	79ZK	P
gl	C	1.0 (NaClO ₄)	25	3.10	83PD	P
gl	M	1.0 (KNO ₃)	25	3.14	67PN	P
gl	C	2.0 (NaClO ₄)	25	3.30	72DC	P
2-Hydroxy-2-phenylpropanoic acid						
gl	C	0.1 (NaClO ₄)	25	3.30	90HW	P
qh	C	1.0 (NaClO ₄)	25	3.30	66TV	P
Hydroxydiphenylacetic acid (benzilic acid, diphenylglycolic acid)						
gl	C	0.2 (KCl)	25	2.82	93MS	P
control met.	?	0.1 (NaClO ₄)	25	2.96	87AI	P

4.1.2 Metal ion complexes

Studies dealing with the complexation of the main group elements have been reported for alkaline earth elements and for lead(II).

The alkaline earth ions all form fairly weak complexes. As such, small values cannot be determined accurately by potentiometric methods, the reported values cannot be recommended, and the data should be regarded as merely indicative. Two papers report equilibrium data for the Pb²⁺ complexes: taking into account the different ionic strength employed, the results are in rather good agreement and can be accepted as provisional. With very few exceptions, isolated values of stability constants are avail-

able for the complexation of transition elements. The spectrophotometric values for the iron(III) complexes are rejected since the experimental conditions are not specified or the hydrolysis of the metal ion cannot be excluded [71SC, 76SC]. The complexation results for Hf^{4+} and Zr^{4+} [76AE] appear doubtful, whereas those of the VO^{2+} complexes, which seem accurately determined, are provisional. Among the divalent transition elements, Cu^{2+} forms the most stable complexes, and the order of increasing stability is : $\text{Mn}^{2+} < \text{Cd}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$.

Table 9 Stability constants of metal complexes of substituted 2-hydroxycarboxylic acids.

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
2-Hydroxy-2-methylpropanoic acid									
Be^{2+}	gl	0.5 (NaClO_4)	25	1.16	2.64			79DT	P
				$\lg K[\text{BeL}^+ = \text{BeH}_{-1}\text{L} + \text{H}^+] = -3.68$					P
				$\lg K[\text{Be}_3(\text{OH})_3^{3+} + 3\text{L}^- = \text{Be}_3(\text{OH})_3\text{L}_3] = -4.68$					P
Mg^{2+}	qh	1.0 (NaClO_4)	25	0.81	1.47			65VT	P
Ca^{2+}	qh	1.0 (NaClO_4)	25	0.92	1.42			65VT	P
Sr^{2+}	qh	1.0 (NaClO_4)	25	0.55	0.73			65VT	P
Ba^{2+}	qh	1.0 (NaClO_4)	25	0.36	0.51			65VT	P
Pb^{2+}	qh	1.0 (NaClO_4)	25	2.03	3.20	3.40		67TG	P
	Pb/Hg	3.0 (NaClO_4)	25	2.23	3.23	3.29		66WB	P
VO^{2+}	gl	0.2 (KCl)	25	3.10(3)	5.89(2)			93MS	P
				$\lg K[\text{VO}^{2+} + \text{L}^- = \text{VOH}_{-1}\text{L} + \text{H}^+] = -1.03$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_{-1}\text{L}_2 + \text{H}^+] = 1.64$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_{-2}\text{L}_2^{2-} + 2\text{H}^+] = -3.03$					P
				$\lg K[\text{VOH}_{-1}\text{L} + \text{L}^- = \text{VOH}_{-1}\text{L}_2^-] = 2.67$					P
Mn^{2+}	qh	1.0 (NaClO_4)	25	0.96	1.54	1.74		67TG	P
Co^{2+}	qh	1.0 (NaClO_4)	25	1.45	2.43	2.73		67TG	P
Ni^{2+}	qh	1.0 (NaClO_4)	25	1.67	2.80	3.20		67TG	P
Cu^{2+}	gl	0.1 (NaClO_4)	25	2.91	4.80			70CB	P
	gl	0.1 (KNO_3)	25	2.82	4.62			74PK	P
	qh	1.0 (NaClO_4)	25	2.74	4.34	4.74		67TG	P
	gl	2.0 (NaClO_4)	20	2.35	3.55			80J	P
	sp	2.0 (NaClO_4)	20	2.43	3.73				P
Zn^{2+}	dis	0.75 (NaClO_4)	25	1.74	2.97			69L	P
	qh	1.0 (NaClO_4)	25	1.70	2.99	3.39		67TG	P
Cd^{2+}	qh	1.0 (NaClO_4)	25	1.24	2.16	2.46		67TG	P
Sc^{3+}	gl	0.1 (KNO_3)	25	4.84				84II	P
Y^{3+}	gl	0.2 (NaClO_4)	25	2.92	5.62	7.34	8.78	64DV	P
	gl	0.5 (NaClO_4)	25	2.88	5.32	6.75		64SP	P
	qh	2.0 (NaClO_4)	25	2.86	5.44	7.30		61CC	P
Ce^{3+}	gl	0.2 (NaClO_4)	25	2.55	4.08	5.49		64DV	P
	gl	0.5 (NaClO_4)	25	2.37	4.01			64SP	P
	dis	1.0 (NaClO_4)	24–25	2.37	3.93	4.85	5.85	67LN	P
	ix	1.0 (NaClO_4)	25	2.36	3.96			67LN	P
	qh	2.0 (NaClO_4)	25	2.43	4.32	5.32		61CC	P

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Table 9 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
Ce^{4+}	kin	1.5 $[(\text{H}^+, \text{Na}^+)\text{ClO}_4]$ pH < 0.5		$\lg K[\text{Ce}^{4+} + \text{HL} = \text{Ce}(\text{HL})^{4+}]$					
			11.3	1.63				77AM	P
			16.1	1.93					P
			20.7	1.89					P
			25	1.74					P
				$\lg K[\text{CeOH}^{3+} + \text{HL} = \text{CeL}^{3+} + \text{H}_2\text{O}]$					
			11.3	3.24					P
			16.1	3.06					P
	20.7	2.84					P		
	25	2.57					P		
	sp	1.5 $[(\text{H}^+, \text{Na}^+)\text{ClO}_4]$ pH < 0.5	$\lg K[\text{Ce}^{4+} + \text{HL} = \text{Ce}(\text{HL})^{4+}]$						
			11.3	1.72				P	
			16.1	1.95				P	
			20.7	1.89				P	
25			1.60				P		
Dy^{3+}	gl	0.2 (NaClO_4)	25	2.94	5.45	7.29	8.50	64DV	P
	gl	0.5 (NaClO_4)	25	2.95	5.32	7.16		64SP	P
Er^{3+}	qh	1.0 (NaClO_4)	25	2.83	5.33	7.05	8.33	64EV	P
	gl	0.2 (NaClO_4)	25	3.01	5.70	7.58	9.03	64DV	P
Eu^{3+}	gl	0.5 (NaClO_4)	25	3.03	5.54	7.56		64SP	P
	qh	2.0 (NaClO_4)	25	3.07	5.73	7.80		61CC	P
	gl	0.2 (NaClO_4)	25	2.79	4.86	6.34	7.59	64DV	P
	gl	0.5 (NaClO_4)	25	2.71	4.92	5.91		64SP	P
	dis	0.5 (NaClO_4)	24–25	2.72	5.08	6.40		66LN	P
Gd^{3+}	ix	0.5 (NaClO_4)	25	2.71	4.97			66LN	P
	qh	2.0 (NaClO_4)	25	2.70	4.94	6.52		61CC	P
	gl	0.2 (NaClO_4)	25	2.79	4.98	6.50	7.65	64DV	P
	gl	0.5 (NaClO_4)	25	2.71	4.97	6.01		64SP	P
Ho^{3+}	qh	2.0 (NaClO_4)	25	2.82	5.15	6.77		61CC	P
	gl	0.2 (NaClO_4)	25	2.98	5.54	7.44	8.74	64DV	P
	gl	0.5 (NaClO_4)	25	2.98	5.42	7.41		64SP	P
La^{3+}	qh	2.0 (NaClO_4)	25	3.05	5.64	7.67		61CC	P
	gl	0.2 (NaClO_4)	25	2.30	4.04			64DV	P
	gl	0.5 (NaClO_4)	25	2.22	3.67			64SP	P
	qh	1.0 (NaClO_4)	25	2.16	3.63	4.38	4.84	64EV	P
Lu^{3+}	qh	2.0 (NaClO_4)	25	2.28	3.98	5.18		66CF	P
	gl	0.2 (NaClO_4)	25	3.18	6.05	8.07	9.99	64DV	P
	gl	0.5 (NaClO_4)	25	3.21	5.85	8.21		64SP	P
Nd^{3+}	gl	0.2 (NaClO_4)	25	2.74	4.42	5.98	6.58	64DV	P
	gl	0.5 (NaClO_4)	25	2.54	4.32			64SP	P
	qh	2.0 (NaClO_4)	25	2.62	4.67	6.07		61CC	P
	qh	2.0 (NaClO_4)	25	2.58	4.57	5.84		66CF	P
	sp	2.0 (NaClO_4)	21	2.62	4.72	5.93	6.89	81BMa	P
Pm^{3+}	ix.pH	0.2 (NaClO_4)	20	2.63	4.78	5.90		68WZ	P
Pr^{3+}	gl	0.2 (NaClO_4)	25	2.59	4.37	5.60	6.38	64DV	P
	ix.pH	0.2 (NaClO_4)	25	2.67	4.85	5.87		68WZ	P
	gl	0.5 (NaClO_4)	25	2.48	4.12			64SP	P

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Table 9 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
Sm^{3+}	gl	0.2 (NaClO ₄)	25	2.75	4.77	6.17	7.38	64DV	P
	gl	0.5 (NaClO ₄)	25	2.63	4.60			64SP	P
	qh	1.0 (NaClO ₄)	25	2.63	4.76	6.09	7.24	64EV	P
	qh	2.0 (NaClO ₄)	25	2.75	4.90	6.48		61CC	P
Tb^{3+}	gl	0.2 (NaClO ₄)	25	2.92	5.24	6.86	8.09	64DV	P
	gl	0.5 (NaClO ₄)	25	2.87	5.21	6.19		64SP	P
	qh	2.0 (NaClO ₄)	25	2.83	5.25	7.03		61CC	P
Tm^{3+}	gl	0.2 (NaClO ₄)	25	3.10	5.79	7.71	9.33	64DV	P
	gl	0.5 (NaClO ₄)	25	3.13	5.62	7.84		64SP	P
	qh	2.0 (NaClO ₄)	25	3.05	5.15			66CF	P
Yb^{3+}	gl	0.1 (NaClO ₄)	25	3.59	6.45	8.90		70CB	P
	gl	0.2 (NaClO ₄)	25	3.13	5.87	7.94	9.72	64DV	P
	gl	0.5 (NaClO ₄)	25	3.18	5.76	8.02		64SP	P
	qh	1.0 (NaClO ₄)	25	3.00	5.79	7.88	9.53	64EV	P
	qh	2.0 (NaClO ₄)	25	3.15	6.00	8.12		61CC	P
Th^{4+}	qh	1.0 (NaClO ₄)	20	4.43	8.15	11.06	13.60	73MB	P
UO_2^{2+}	qh	1.0 (NaClO ₄)	25	3.02	4.85	6.39		67TG	P
	gl	1.0 (NaClO ₄)	20	3.18	5.13	6.67		74MT	P
NpO_2^+	dis	1.0 (NaClO ₄)	25	1.73	2.46			92TI	P
	sp	2.0 (NaClO ₄)	25	1.80				90RN	P
NpO_2^{2+}	gl	1.0 (NaClO ₄)	20	3.15	5.25			74MT	P
PuO_2^{2+}	gl	1.0 (NaClO ₄)	20	3.04	5.00	6.00		74MT	P
2-Hydroxy-2-methylbutanoic acid									
VO^{2+}	gl	0.2 (KCl)	25	2.88	5.55			93MS	P
				$\lg K[\text{VO}^{2+} + \text{L}^- = \text{VOH}_{-1}\text{L} + \text{H}^+] = -1.15$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_{-1}\text{L}_2^{2-} + \text{H}^+] = 1.19$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_2\text{L}_2^{2-} + 2\text{H}^+] = -2.97$					P
				$\lg K[\text{VOH}_{-1}\text{L} + \text{L}^- = \text{VOH}_{-1}\text{L}_2^-] = 2.34$					P
Ce^{3+}	gl	0.1 (KNO ₃)	25	2.51	4.23	5.43		69PC	P
Dy^{3+}	gl	0.1 (KNO ₃)	25	3.16	5.70	7.42		69PC	P
	qh	1.0 (NaClO ₄)	25	3.03	5.51	7.17	8.54	64EV	P
Er^{3+}	gl	0.1 (KNO ₃)	25	3.32	6.05	8.03		69PC	P
Eu^{3+}	gl	0.1 (KNO ₃)	25	2.90	5.20	6.80		69PC	P
Gd^{3+}	gl	0.1 (KNO ₃)	25	2.94	5.28	6.86		69PC	P
Ho^{3+}	gl	0.1 (KNO ₃)	25	3.24	5.87	7.72		69PC	P
La^{3+}	gl	0.1 (KNO ₃)	25	2.34	3.92	5.22		69PC	P
	qh	1.0 (NaClO ₄)	25	2.01	3.27	3.89		64EV	P
Lu^{3+}	gl	0.1 (KNO ₃)	25	3.45	6.30	8.35		69PC	P
Nd^{3+}	gl	0.1 (KNO ₃)	25	2.65	4.49	5.81		69PC	P
Pr^{3+}	gl	0.1 (KNO ₃)	25	2.54	4.31	5.42		69PC	P
Sm^{3+}	gl	0.1 (KNO ₃)	25	2.80	4.95	6.46		69PC	P
	qh	1.0 (NaClO ₄)	25	2.60	4.74	6.00	7.14	64EV	P
Tb^{3+}	gl	0.1 (KNO ₃)	25	3.10	5.58	7.31		69PC	P
Tm^{3+}	gl	0.1 (KNO ₃)	25	3.37	6.13	8.05		69PC	P
Yb^{3+}	gl	0.1 (KNO ₃)	25	3.43	6.26	8.29		69PC	P
	qh	1.0 (NaClO ₄)	25	3.20	5.87	7.85	9.27	64EV	P
NpO_2^+	dis	1.0 (NaClO ₄)	25	1.60	2.21			83IT	P
	dis	1.0 (NaClO ₄)	25	1.77	2.25			92TI	P

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Table 9 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
2-Ethyl-2-hydroxybutanoic acid									
VO^{2+}	gl	0.2 (KCl)	25	2.61	5.05			93MS	P
				$\lg K[\text{VO}^{2+} + \text{L}^- = \text{VOH}_{-1}\text{L} + \text{H}^+] = -1.09$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_{-1}\text{L}_2^- + \text{H}^+] = 1.03$					P
				$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_2\text{L}_2^{2-} + 2\text{H}^+] = -2.85$					P
				$\lg K[\text{VOH}_{-1}\text{L} + \text{L}^- = \text{VOH}_{-1}\text{L}_2^-] = 2.12$					P
Er^{3+}	qh	1.0 (NaClO_4)	25	3.11	5.27	6.60	7.55	65TV	P
Gd^{3+}	qh	1.0 (NaClO_4)	25	2.71	4.65	5.63	6.49	65TV	P
Ho^{3+}	qh	1.0 (NaClO_4)	25	3.11	5.25	6.71	7.43	65TV	P
La^{3+}	qh	1.0 (NaClO_4)	25	1.85	3.11	3.67	4.09	65TV	P
Nd^{3+}	qh	1.0 (NaClO_4)	25	2.28	3.89	5.10	6.04	65TV	P
Pr^{3+}	qh	1.0 (NaClO_4)	25	2.31	3.80	4.82	5.39	65TV	P
Tb^{3+}	qh	1.0 (NaClO_4)	25	3.01	5.08	6.45	6.98	65TV	P
Yb^{3+}	qh	1.0 (NaClO_4)	25	3.10	5.36	6.67	7.76	65TV	P
2-Hydroxy-2,3-dimethylbutanoic acid									
Eu^{3+}	qh	1.0 (NaClO_4)	25	2.68	4.65	6.06	7.05	65TV	P
Gd^{3+}	qh	1.0 (NaClO_4)	25	2.65	4.70	6.04	6.98	65TV	P
Ho^{3+}	qh	1.0 (NaClO_4)	25	3.02	5.37	6.90	8.24	65TV	P
Nd^{3+}	qh	1.0 (NaClO_4)	25	2.57	4.28	5.52	6.59	65TV	P
Pr^{3+}	qh	1.0 (NaClO_4)	25	2.25	3.87	4.87	5.69	65TV	P
Yb^{3+}	qh	1.0 (NaClO_4)	25	3.12	5.56	7.21	8.60	65TV	P
2-Ethyl-2-hydroxy-3-methylbutanoic acid									
Y^{3+}	gl	0.1 (NaClO_4)	25	2.78	4.52			76SP	P
Ce^{3+}	gl	0.1 (NaClO_4)	25	1.91	3.02			76SP	P
Dy^{3+}	gl	0.1 (NaClO_4)	25	2.86	4.68			76SP	P
Er^{3+}	gl	0.1 (NaClO_4)	25	2.95	4.81			76SP	P
Eu^{3+}	gl	0.1 (NaClO_4)	25	2.62	4.27			76SP	P
Gd^{3+}	gl	0.1 (NaClO_4)	25	2.68	4.38			76SP	P
Ho^{3+}	gl	0.1 (NaClO_4)	25	2.87	4.73			76SP	P
La^{3+}	gl	0.1 (NaClO_4)	25	1.75	2.97			76SP	P
Lu^{3+}	gl	0.1 (NaClO_4)	25	3.03	4.86			76SP	P
Nd^{3+}	gl	0.1 (NaClO_4)	25	2.08	3.54			76SP	P
Pr^{3+}	gl	0.1 (NaClO_4)	25	1.97	3.17			76SP	P
Sm^{3+}	gl	0.1 (NaClO_4)	25	2.44	4.17			76SP	P
Tb^{3+}	gl	0.1 (NaClO_4)	25	2.81	4.60			76SP	P
Tm^{3+}	gl	0.1 (NaClO_4)	25	2.99	4.88			76SP	P
Yb^{3+}	gl	0.1 (NaClO_4)	25	3.02	4.92			76SP	P
2-Hydroxy-2-methylpentanoic acid									
Ce^{3+}	qh	1.0 (NaClO_4)	25	2.21	3.87	4.90	5.71	64EV	P
Dy^{3+}	qh	1.0 (NaClO_4)	25	3.00	5.47	7.33	8.45	64EV	P
La^{3+}	qh	1.0 (NaClO_4)	25	2.20	3.45	4.22		64EV	P
Nd^{3+}	qh	1.0 (NaClO_4)	25	2.38	4.23	5.40	6.46	64EV	P
Sm^{3+}	qh	1.0 (NaClO_4)	25	2.59	4.71	6.21	7.07	64EV	P
Yb^{3+}	qh	1.0 (NaClO_4)	25	3.29	5.84	8.05	9.17	64EV	P

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Table 9 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category	
2-Hydroxy-2,4-dimethylpentanoic acid										
Ce ³⁺	qh	1.0 (NaClO ₄)	25	2.23	3.57	4.88		65TV	P	
Dy ³⁺	qh	1.0 (NaClO ₄)	25	3.18	5.64	7.39	8.57	65TV	P	
Er ³⁺	qh	1.0 (NaClO ₄)	25	3.24	5.87	7.76	8.85	65TV	P	
Eu ³⁺	qh	1.0 (NaClO ₄)	25	2.71	5.06	6.43	7.68	65TV	P	
Gd ³⁺	qh	1.0 (NaClO ₄)	25	2.77	5.13	6.52	7.66	65TV	P	
La ³⁺	qh	1.0 (NaClO ₄)	25	2.07	3.37	4.47		65TV	P	
Nd ³⁺	qh	1.0 (NaClO ₄)	25	2.53	4.42	5.74		65TV	P	
Pr ³⁺	qh	1.0 (NaClO ₄)	25	2.51	4.03	5.51		65TV	P	
Sm ³⁺	qh	1.0 (NaClO ₄)	25	2.71	4.90	6.38	7.40	65TV	P	
Yb ³⁺	qh	1.0 (NaClO ₄)	25	3.21	5.95	7.70	9.10	65TV	P	
2-Hydroxy-2-propylpentanoic acid										
Dy ³⁺	qh	1.0 (NaClO ₄)	25	3.08	5.57			65TV	P	
Er ³⁺	qh	1.0 (NaClO ₄)	25	3.29	5.53	7.67		65TV	P	
Eu ³⁺	qh	1.0 (NaClO ₄)	25	2.81	4.99			65TV	P	
Gd ³⁺	qh	1.0 (NaClO ₄)	25	2.83	5.03			65TV	P	
Nd ³⁺	qh	1.0 (NaClO ₄)	25	2.61	4.37			65TV	P	
Pr ³⁺	qh	1.0 (NaClO ₄)	25	2.53	3.98			65TV	P	
Sm ³⁺	qh	1.0 (NaClO ₄)	25	2.65	4.82			65TV	P	
Yb ³⁺	qh	1.0 (NaClO ₄)	25	3.36	5.59	7.73		65TV	P	
2-Hydroxy-2-phenylacetic acid (mandelic acid)										
Ca ²⁺	sol	0.0	25	1.46				38D	P	
		0.0	25	1.46				75DN	P	
				30	1.58				P	
				35	1.62				P	
				40	1.75				P	
				45	1.83				P	
In ³⁺	dis	0.5 (NaClO ₄)	25	2.58	5.40			70T	P	
	gl	0.2 (KCl)	25	2.60				93MS	P	
								$\lg K[\text{VO}^{2+} + \text{L}^- = \text{VOH}_{-1}\text{L} + \text{H}^+] = -1.04$	P	
								$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_{-1}\text{L}_2^- + \text{H}^+] = 1.52$	P	
								$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_{-2}\text{L}_2^{2-} + 2\text{H}^+] = 3.10$	P	
								$\lg K[\text{VOH}_{-1}\text{L} + \text{L}^- = \text{VOH}_{-1}\text{L}_2^-] = 2.66$	P	
Co ²⁺	kin	0.5 (KNO ₃)	25					$\lg K[\text{VO}^{2+} + \text{HL}^- = \text{VOL} + \text{H}^+] = -2.21$	80CK	P
	gl	2.0 (NaClO ₄)	20	1.22	1.74	2.67		68FL	R	
	CD	2.0 (NaClO ₄)	20	1.23	1.15(D)	2.76		68FL	R	
	gl	2.0 (NaClO ₄)	25	1.19	2.07			85MF	R	
	qh	2.0 (NaClO ₄)	25	1.26	1.95			85MF	R	
Ni ²⁺	gl	0.5 (KNO ₃)	25	1.66				81CK	P	
	kin	0.5 (KNO ₃)	25	1.62				81CK	P	
	gl	2.0 (NaClO ₄)	20	1.41	2.26	2.90		68FL	R	
	CD	2.0 (NaClO ₄)	20	1.38	2.04	2.95		68FL	R	
	gl	2.0 (NaClO ₄)	25	1.31	2.48			85MF	R	
Cu ²⁺	qh	2.0 (NaClO ₄)	25	1.35	2.40			85MF	R	
	gl	1.0 (NaClO ₄)	25	2.70				83PD	P	

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Table 9 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
Zn ²⁺	CD	2.0 (NaClO ₄)	20	1.48	2.42	3.59		65LF	P
	gl	2.0 (NaClO ₄)	20	1.51	2.58	3.36		68FL	P
Zn ²⁺	gl	2.0 (NaClO ₄)	25	1.36	2.58			85MF	P
	qh	2.0 (NaClO ₄)	25	1.40	2.45			85MF	P
MoO ₄ ²⁻	nmr	≈1.0 (NaCl)	21					87CR	
				$\lg K[\text{MoO}_4^{2-} + 2\text{L} + 2\text{H}^+ = \text{MoO}_2\text{H}_{-2}\text{L}_2 + 2\text{H}_2\text{O}] = 14.8$					P
Sc ³⁺	gl	0.1 (KNO ₃)	25	2.91				84II	P
Ce ³⁺	gl	2.0 (NaClO ₄)	25	2.17				72DC	P
Ce ⁴⁺	kin	1.5 [(H ⁺ ,Na ⁺)ClO ₄] pH < 0.5		$\lg K[\text{Ce}^{4+} + \text{HL} = \text{Ce}(\text{HL})^{4+}]$					
			6.4	1.82				77AM	P
			12.5	1.60					P
			17.5	1.88					P
Ce ⁴⁺	kin	1.5 [(H ⁺ ,Na ⁺)ClO ₄] pH < 0.5		$\lg K[\text{CeOH}^{3+} + \text{HL} = \text{CeL}^{3+} + \text{H}_2\text{O}]$				77AM	
			6.4	3.30					P
			12.5	3.08					P
			17.5	2.81					P
Dy ³⁺	gl	0.1 (NaClO ₄)	25	3.03	5.29			89HM	P
	gl	2.0 (NaClO ₄)	25	2.57				72DC	P
Er ³⁺	gl	0.1 (NaClO ₄)	25	3.15	5.41			89HM	P
	gl	2.0 (NaClO ₄)	25	2.68				72DC	P
Eu ³⁺	dis	0 corr	25	3.37	6.21			67M	P
	dis	0.05 (NaClO ₄)	25	2.87	5.10			67M	P
	dis	0.1 (NaClO ₄)	25	2.70	4.90			67M	P
	gl	0.1 (NaClO ₄)	25	2.95	5.07			89HM	P
	gl	2.0 (NaClO ₄)	25	2.25				72DC	P
Gd ³⁺	gl	0.1 (NaClO ₄)	25	2.88	5.01			89HM	P
	gl	2.0 (NaClO ₄)	25	2.42				72DC	P
Ho ³⁺	gl	0.1 (NaClO ₄)	25	3.05	5.35			89HM	P
	gl	2.0 (NaClO ₄)	25	2.54				72DC	P
La ³⁺	gl	0.1 (NaClO ₄)	25	2.55	4.14			89HM	P
	gl	2.0 (NaClO ₄)	25	1.93				72DC	P
Lu ³⁺	gl	0.1 (NaClO ₄)	25	3.25	5.83			89HM	P
	gl	2.0 (NaClO ₄)	25	2.77				72DC	P
Nd ³⁺	gl	0.1 (NaClO ₄)	25	2.83	4.77			89HM	P
	gl	2.0 (NaClO ₄)	25	2.43				72DC	P
Pr ³⁺	gl	0.1 (NaClO ₄)	25	2.76	4.65			89HM	P
	gl	2.0 (NaClO ₄)	25	2.30				72DC	P
Sm ³⁺	gl	0.1 (NaClO ₄)	25	2.90	4.75			89HM	P
	gl	2.0 (NaClO ₄)	25	2.47				72DC	P
Tb ³⁺	gl	0.1 (NaClO ₄)	25	3.01	5.25			89HM	P
	gl	2.0 (NaClO ₄)	25	2.52				72DC	P
Tm ³⁺	gl	0.1 (NaClO ₄)	25	3.20	5.56			89HM	P
	gl	2.0 (NaClO ₄)	25	2.71				72DC	P
Yb ³⁺	gl	0.1 (NaClO ₄)	25	3.29	5.76			89HM	P
	gl	2.0 (NaClO ₄)	25	2.72				72DC	P
Th ⁴⁺	qh	1.0 (NaClO ₄)	20	3.88	6.89	9.69	11.98	73MB	P
UO ₂ ²⁺	gl	1.0 (NaClO ₄)	20	2.57	4.10	5.32		74MT	P

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Table 9 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	Reference	Category
2-Hydroxy-2-phenylpropanoic acid (atrolactic acid)									
Dy ³⁺	gl	0.1 (NaClO ₄)	25	3.24	5.67			90HW	P
Er ³⁺	gl	0.1 (NaClO ₄)	25	3.34	5.88			90HW	P
	qh	1.0 (NaClO ₄)	25	3.03	5.51	7.52	9.42	66TV	P
Eu ³⁺	gl	0.1 (NaClO ₄)	25	2.99	5.11			90HW	P
	qh	1.0 (NaClO ₄)	25	2.55	4.72			66TV	P
Gd ³⁺	gl	0.1 (NaClO ₄)	25	2.98	5.23			90HW	P
	qh	1.0 (NaClO ₄)	25	2.54	4.61	6.31	7.64	66TV	P
Ho ³⁺	gl	0.1 (NaClO ₄)	25	3.28	5.64			90HW	P
	qh	1.0 (NaClO ₄)	25	2.97	5.35	7.27	9.03	66TV	P
La ³⁺	gl	0.1 (NaClO ₄)	25	2.49	4.43			90HW	P
Lu ³⁺	gl	0.1 (NaClO ₄)	25	3.40	6.27			90HW	P
Nd ³⁺	gl	0.1 (NaClO ₄)	25	2.70	4.57			90HW	P
	qh	1.0 (NaClO ₄)	25	2.55	4.19	5.61	6.82	66TV	P
Pr ³⁺	gl	0.1 (NaClO ₄)	25	2.70	4.39			90HW	P
	qh	1.0 (NaClO ₄)	25	2.40	3.96	5.32	6.24	66TV	P
Sm ³⁺	gl	0.1 (NaClO ₄)	25	2.89	4.99			90HV	P
	qh	1.0 (NaClO ₄)	25	2.57	4.46	6.00	7.31	66TV	P
Tb ³⁺	gl	0.1 (NaClO ₄)	25	3.17	5.45			90HV	P
Tm ³⁺	gl	0.1 (NaClO ₄)	25	3.22	6.04			90HW	P
Yb ³⁺	gl	0.1 (NaClO ₄)	25	3.42	6.29			90HW	P
	qh	1.0 (NaClO ₄)	25	3.05	5.61	7.68	9.54	66TV	P
2-Hydroxy-3-phenylpropanoic acid									
MoO ₄ ²⁻	nmr	≈1.0 (NaCl)	21					87CR	P
								$\lg K[\text{MoO}_4^{2-} + 2\text{L}^- + 2\text{H}^+ = \text{MoO}_2\text{H}_2\text{L}_2^{2-} + 2\text{H}_2\text{O}] = 16.0$	
WO ₄ ²⁻	nmr	≈1.0 (NaCl)	21					87CR	P
								$\lg K[\text{WO}_4^{2-} + 2\text{L}^- + 2\text{H}^+ = \text{WO}_2\text{H}_2\text{L}_2^{2-} + 2\text{H}_2\text{O}] = 15.8$	
Hydroxydiphenylacetic acid (benzilic acid, diphenylglycolic acid)									
Fe ³⁺	kin	1.0 (NaClO ₄)	25					$\lg K[\text{Fe}^{3+} + \text{HL} = \text{FeH}_1\text{L}^+ + 2\text{H}^+] = -0.4779\text{M}$	P
VO ²⁺	gl	0.2 (KCl)	25	2.29				93MS	P
								$\lg K[\text{VO}^{2+} + \text{L}^- = \text{VOH}_1\text{L}_2^- + \text{H}^+] = -0.92$	P
								$\lg K[\text{VO}^{2+} + 2\text{L}^- = \text{VOH}_1\text{L}_2^{2-} + \text{H}^+] = 1.63$	P
								$\lg K[\text{VO}^{2+} + \text{L}^{2-} = \text{VOH}_2\text{L}_2^{2-} + 2\text{H}^+] = -1.90$	P
								$\lg K[\text{VOH}_1\text{L}^- = \text{VOH}_1\text{L}_2] = 2.55$	P

The complexes of the trivalent rare earth ions have been the most thoroughly investigated of any other metal ion, and several papers have been published on these systems.

The stability constants of 64DV and 64SP appear accurately determined, are in fairly good agreement with each other (taking into account the slightly different ionic strengths used), and are then provisional. The potentiometric values of 61CC appear also accurately determined and are regarded as provisional. The ion-exchange values of 60SV for the Ce³⁺ complexes are rejected, first of all because too few experimental details are given and secondly because the authors obtain the same values of stability constants for the complexes with glycolic, lactic, and α -hydroxyisobutyric acids, whereas it has been demonstrated that the stability of the lanthanide(III) complexes with these ligands increases in the order: glycolate < lactate < α -hydroxyisobutyrate. Also questionable are the values of 71S for the Ce³⁺ and Pm³⁺. In the paper, there is no mention of the background electrolyte used, and, more important, the pH range investigated, 1–11, does not exclude the possibility of hydrolysis of the metal ions and/or of the complexes. The values obtained by the ion-exchange method [68A, 68Aa] and by the distribu-

tion method [71A] for the Eu^{3+} and Tb^{3+} complexes cannot be accepted as the temperature is not clearly specified in the investigation. The experimental conditions are not specified in 67DV for the Pm^{3+} complexes, and the value is rejected. The remaining values are all provisional.

A few reports are available for actinide complexation. Two papers report data on the Th^{4+} complexes: the ion-exchange values of 63LG are rejected because the constants were determined at ligand concentration too high for the method used and because the experimental conditions are not well specified. The stability constants reported by 73MB are provisional.

As for the uranyl(VI) complexes, the value of 62SB has been determined at a pH value too high to exclude hydrolysis of the metal ion. The constants are all rather high and are rejected. The other data are provisional.

Four papers report equilibrium data for the neptunium(V) complexes. Three of them are from the same group and are rather discordant [71M, 82IT, 83IT]. The remaining ones [90RN, 92TI] are acceptable and thus provisional.

The accurately determined formation constants of the neptunium(VI) and plutonium(VI) complexes reported by 74MT are provisional.

Insufficient details on the experimental conditions used make the results for the remaining actinides unreliable, and the reported data are rejected [70AL, 71S].

4.2 2-Hydroxy-2-methylbutanoic acid

4.2.1 Protonation constants

Two independent measurements have been reported at 0.1 and 0.2 mol dm⁻³ ionic strengths at 25 °C. The measurements have been carried out accurately, and the constants are regarded as provisional.

4.2.2 Metal ion complexes

The available data are rather few, and the majority deals with the lanthanide(III) complexation.

The results of the potentiometric investigation of 93MS on the VO^{2+} complexes are reliable, and the stability constants are provisional.

Three sets of data are available for the lanthanide(III) complexes. The stability constants of 91BV, obtained by the electromigration method, for the Dy^{3+} and Ho^{3+} complexes are too high, have rather large deviations, and the pH of the solutions is rather high so that the hydrolysis of the ions cannot be excluded. The results are unreliable and, therefore, rejected. The potentiometric values of 64EV and 69PC are accurately determined and are regarded as provisional.

Three papers, from the same research group, have been published on the NpO_2^+ complexes. The results of 82IT are rejected because the experimental conditions during the measurements are not controlled. The remaining values are provisional.

4.3 2-Hydroxy-3-methylbutanoic acid

4.3.1 Protonation constants

The protonation constant has been determined, at three different temperatures, by conductivity measurements. The values are of the order of magnitude expected as the methyl group is moved away from the carboxyl group and are provisional.

4.3.2 Metal ion complexes

The results concerning the complexes of cerium(III) and yttrium(III) are unreliable for the same reasons mentioned in the evaluation of the complexes of these ions with α -hydroxyisobutanoic acid [60SV].

4.4 2-Ethyl-2-hydroxybutanoic acid

4.4.1 Protonation constants

Only in two papers have values for the protonation constant of 2-ethyl-2-hydroxybutanoic acid been reported. Based on the trend observed for the protonation constants of substituted hydroxycarboxylic acids, the reported values are of the expected order of magnitude and have been evaluated as provisional.

4.4.2 Metal ion complexes

The data in Table 9 show that complex formation constants are available for a few elements: vanadium(IV), some lanthanides(III), and neptunium(V). With this ligand, the VO^{2+} forms the same species as with 2-hydroxy-2-methylbutanoic acid. The formation constants with the latter ligand are higher as expected given its higher basicity. The results are provisionally accepted.

The stability constants of the lanthanide(III) complexes appear reliable and are provisional, whereas those for the NpO_2^+ ion are rejected [82IT, 83IT].

4.5 2-Hydroxy-2-methyl- and 2-hydroxy-2-propylpentanoic acids

4.5.1 Protonation constants

For the first acid, no protonation constant values are available. For the other ligand, a single protonation constant value has been reported. The value is of the expected order of magnitude and is provisional.

4.5.2 Metal ion complexes

The very few equilibrium data for these ligands found in the literature deal with the complexation of a restricted number of lanthanides(III) ions. The stability constants seem accurately determined and are regarded as provisional.

4.6 2-Ethyl-2-hydroxy-3-methylbutanoic acid

4.6.1 Protonation constants

The protonation constant of this ligand is of the same order of magnitude of 2-ethyl-2-hydroxybutanoic acid, indicating that the alkyl group in the 3-position has little or no influence on the dissociation of the carboxyl group. The value is considered as provisional.

4.6.2 Metal ion complexes

The only equilibrium data available for this ligand are those reported by 76SP on the complexation of trivalent rare earths.

The stability constants of the lanthanide(III) complexes are considerably lower than those of other α -hydroxycarboxylic acids of comparable basicity and show a remarkable increase with increasing atomic number from lanthanum to gadolinium and a considerably reduced increase for the heavier elements. The trend is likely due to the steric effect of the larger molecule of the ligand on the cations of smaller size.

The results appear reliable, accurately determined, and are provisional.

4.7 2-Hydroxy-2,3-dimethylbutanoic and 2-hydroxy-2,4-dimethylpentanoic acids

4.7.1 Protonation constants

For these two ligands, the available data are from the same research group.

There is very little to be said about these data. The protonation constants appear accurately determined, are of the order of magnitude expected, and are provisional.

4.7.2 Metal ion complexes

The only metal ion complexes studied are those of lanthanides(III). The formation constants are regarded as provisional.

4.8 2-Hydroxy-2-phenylacetic acid (mandelic acid)

4.8.1 Protonation constants

Several papers report data on the protonation of this ligand.

Most of the data appear reliable and are recommended or provisional. Some values [67VA, 73RM, 76SSa, 77JK, 78JS, 82RP, 85KM] are rejected either because too few experimental details are given or because the values are too high or too low compared with those reported by other authors.

4.8.2 Metal ion complexes

The ion-exchange value of 65BK for the Be^{2+} complexes cannot be accepted because the high pH value used does not exclude hydrolytic processes. The formation constants for the Ca^{2+} complexes, determined by solubility measurements [75DN], should be regarded as provisional. Of the other elements of the main group, data are available for the complexes of indium(III). The values of 75CS are rejected because they are too high, those of 76SSa because of insufficient experimental details reported in the paper. The values of 70T should be regarded as provisional.

Too few details and the lack of duplicate results make the results of 75KA for the Mn^{2+} and Fe^{2+} complexes unacceptable. In addition, for the Fe^{3+} complexes the experimental conditions are not well specified.

Most of the data on the complexes of the divalent transition-metal ions Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} are from the same group [70KA, 72KA, 73KA, 75KA]. In addition to the insufficient experimental details, the reported stability constants are extremely high and, therefore, rejected. In addition, the data of 61BB, 70KK, 76SC, 80CKa, and 83US are not accepted. The complexes of Co^{2+} , Ni^{2+} , and Zn^{2+} have been studied by 65LF and 68FL by circular dichroism. The obtained values are well supported by the potentiometric values of 85MF and are recommended or provisional. The potentiometric and kinetic values of 81CK for the Ni^{2+} complexes are regarded as provisional.

Few studies exist on the formation of mandelate complexes with copper(II). The few available data are rejected because of the lack of experimental details [70KA, 75KA] or because the experimental conditions were not well established [83US]. The only acceptable result is that of 83PD, which is provisional.

Only one paper reports data for the Cd^{2+} complexes. The experimental conditions are not clearly defined, and the reported constant is rejected [80CKa].

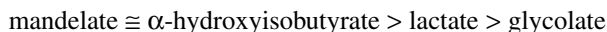
Several papers have been published on the complexation of trivalent lanthanide cations with mandelic acid. As already mentioned, the reason for these investigations is to be found in the use of α -hydroxycarboxylic acids as eluants for the separation of mixtures of trivalent rare earth elements by chromatography.

The available data show that the stability constants of the lanthanide complexes vary with the ionic strength, as already observed for the other α -hydroxycarboxylic acids. The variation is rather marked between 0.1 and 1.0 mol dm^{-3} ionic strength, and becomes rather small between 1.0 and 2.0 mol dm^{-3} . The order of complexing strength of α -hydroxycarboxylic acids with lanthanides(III) is:



As for the literature data, the stability constants values of 67PN in 0.1 mol dm^{-3} (KNO_3) should be taken with some caution, and those in 1.0 mol dm^{-3} (KNO_3) cannot be accepted, since in this ionic medium the ratio $[\text{LnNO}_3^{2+}]/[\text{Ln}^{3+}]$ is close to unity [65CS] and the authors do not take into consideration the formation of nitrate complexes of lanthanides. As a consequence, the obtained stability constants are lower and are rejected.

Also, the stability constants determined by 66TV should be rejected as the authors find a stability order:



opposite to the commonly accepted trend observed by other authors.

The values reported for Sc^{3+} [66KZ], Y^{3+} [82RP], and lanthanides [68WZ, 82KM] cannot be accepted. The remaining values are considered as provisional.

Of the other results recorded in Table 9, those of 63LG for the thorium complexes are rejected as the experimental conditions are not well specified. Also, the values reported for uranium(VI) cannot be accepted [67VA].

The remaining values are evaluated provisional.

4.9 2-Hydroxy-2-phenylpropanoic acid (atrolactic acid)

4.9.1 Protonation constants

Two independent measurements report values of the protonation constants, which are of the expected order of magnitude and are provisional.

4.9.2 Metal ion complexes

Equilibrium data on the complexation of metal ions with this ligand have been reported for iron(III) and lanthanide(III) ions.

The data for the Fe^{3+} complexes are rejected as the experimental conditions are not well specified [71SC, 76SC].

Data on the complexation of lanthanide(III) ions have been reported in three papers. The values of 66TV and 93HY are evaluated as provisional, those of 68WZ for the Pm^{3+} and Pr^{3+} complexes appear somewhat low and should be rejected.

The available data show that the lanthanide complexes with atrolactate are a little more stable than the complexes with mandelate, as expected given the slightly different basicities of the ligands, and the decrease in the stability of the complexes as the ionic strength increases.

4.10 Hydroxydiphenylacetic acid (benzilic acid, diphenylglycolic acid)

4.10.1 Protonation constants

A single value of protonation constant has been found in the literature [93MS]. The acidity of the carboxyl group is strongly increased by the presence of two phenyl groups in the α -position. The $\text{p}K_{\text{a}}$ is of the expected order of magnitude, appears to be accurately determined, and is provisional.

4.10.2 Metal ion complexes

The data reported for the VO^{2+} ion [93MS] as well as those for Fe^{3+} [79M] are provisional, and those for the Pm^{3+} and Pr^{3+} ions should be rejected [68WZ].

5. ENTHALPY CHANGES OF COMPLEXATION

The protonation enthalpies of 2-hydroxocarboxylic acids and the enthalpy changes of metal complex formation with these ligands have been obtained by direct calorimetric measurements or calculated from stability constants determined over a more or less large temperature range. Both methods have some drawbacks, but enthalpy values obtained by calorimetry are to be considered as the most accurate and reliable.

5.1 Protonation enthalpy changes

Protonation enthalpy changes are available only for glycolic, lactic, mandelic, and atrolactic acids. The enthalpy values have been obtained, at different ionic strengths, both from calorimetric measurements and from protonation constants measured at several temperatures. The corresponding values are listed in Table 10.

For glycolic acid, the calorimetric value at zero ionic strength and 25 °C is in fairly good agreement with that obtained by the temperature variation method. These values are provisional. The value at 1.0 mol dm⁻³ ionic strength appears accurately determined and is also provisional.

As for lactic acid, the calorimetric value of 78FB is in considerable disagreement with those obtained by temperature variation studies. The reported value is rejected as the authors admit that the uncertainty in the experimental data is rather large and that the reliability of the obtained protonation enthalpy is rather low [78FB]. The remaining values are to be considered as provisional.

Table 10 Protonation enthalpy changes of 2-hydroxycarboxylic acids.

Ligand	Method	I_c/M	$t/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	Reference	Category	
2-Hydroxyacetic acid (glycolic acid)							
T	0.0		0.3	-4.268	36N	P	
			12.5	-2.761		P	
			25	-0.879		P	
			37.5	1.339		P	
			50	3.849		P	
	cal ^a	0.0		25	-0.46	67CI	P
				cal ^a	0.0		
	25	-0.63	P				
	40	1.63	P				
	T	0.1 (KNO ₃)		25	-1.5	94PR	P
cal	1.0 (NaClO ₄)		25	-1.63	76DB	P	
2-Hydroxypropanoic acid (lactic acid)							
T	→ 0		0	-3.22	37MT	P	
			10	-1.92		P	
			20	-0.41		P	
			25	0.43		P	
			30	1.32		P	
			35	2.27		P	
			50	5.49		P	
			25	2.9		94PR	P
2-Hydroxy-2-phenylacetic acid (mandelic acid)							
cal	0.1 (NaClO ₄)		25	1.4	93HY	P	
cal	2.0 (NaClO ₄)		25	0.2	72DC	P	
2-Hydroxy-2-phenylpropanoic acid (atrolactic acid)							
cal	0.1 (NaClO ₄)		25	0.07	93HY	P	

^a K_{HL} from 36N.

The protonation enthalpy of mandelic acid has been reported in two papers only. In both cases, the calorimetric method was used, and the results are evaluated as provisional.

A single calorimetric value has been found in the literature for atrolactic acid, and this is provisional.

5.2 Metal complex enthalpy changes

The literature values of the enthalpy changes accompanying metal ion complex formation with 2-hydroxycarboxylic acids are given in Table 11. Enthalpy data are available only for the following hydroxycarboxylate anions: glycolate, lactate, 2-hydroxyisobutyrate, mandelate, and atrolactate. A thorough evaluation of the enthalpy values of metal complexes with these ligands is rendered difficult by the lack, in general, of duplicate results.

An inspection of the enthalpy values reported in Table 11 shows that the majority of the data refer to glycolic and lactic acids and that, among the metal ions, the lanthanides(III), for the reasons mentioned above (see Section 3.1), are the most studied.

Table 11 Enthalpy changes in the formation of metal complexes with 2-hydroxycarboxylic acids (kJ mol^{-1}).

Metal	Method	I_c/M	$t/^\circ\text{C}$	ΔH_1	ΔH_2	ΔH_3	ΔH_4	Reference	Category
2-Hydroxyacetic acid (glycolic acid)									
Ca^{2+}	T	0.0	25	35.5				75DN	P
In^{3+}	T	0.2 (NaClO_4)	35	13.0	22.2			73SM	P
VO^{2+}	cal	1.0 (NaClO_4)	25	-0.59	6.40	4.39		88DT	P
Cu^{2+}	T	0.0	25	-24.5				75DN	P
	cal ^a	1.0 (NaNO_3)	25	-1.46	-3.01			74A	P
Y^{3+}	cal ^b	2.0 (NaClO_4)	25	-0.31	-0.72	-3.74	-3.85	64G	P
	cal ^c	2.0 (NaClO_4)	25	-0.63	-1.67	-6.78		66CF	P
	cal ^b	2.0 (NaClO_4)	25	-3.39	-6.69	-9.49	-12.5	64G	P
Ce^{4+}	T	1.5 (ClO_4^-) ($0.6 \text{H}^+ + 0.9 \text{Na}^+$)	25	$\lg K[\text{Ce}(\text{OH})^{3+} + \text{HL} = \text{CeL}^{3+} + \text{H}_2\text{O}] - 61.9$				77AM	P
Dy^{3+}	cal ^b	2 (NaClO_4)	25	-0.69	-2.54	-7.27	-10.8	64G	P
	cal	2.0 (NaClO_4)	25	-0.33	-4.39			66CF	P
Er^{3+}	cal ^b	2.0 (NaClO_4)	25	-0.80	-2.51	-5.36	-5.98	64G	P
	cal	2.0 (NaClO_4)	25	-0.38	-2.01			66CF	P
Eu^{3+}	cal ^c	2.0 (NaClO_4)	25	-3.5	-7.28			66CF	P
Gd^{3+}	cal ^c	2.0 (NaClO_4)	25	-2.59	-7.57			66CF	R
Ho^{3+}	cal ^c	2.0 (NaClO_4)	25	-0.33	-2.01	-12.05		66CF	P
La^{3+}	cal ^b	2.0 (NaClO_4)	25	-2.65	-4.41	-7.03	-9.16	64G	P
	cal	2.0 (NaClO_4)	25	-3.56	-4.52			66CF	P
Lu^{3+}	cal	2.0 (NaClO_4)	25	-2.72	-5.19			66CF	P
Nd^{3+}	cal ^b	2.0 (NaClO_4)	25	-4.99	-9.15	-14.56	-16.7	64G	P
	cal	2.0 (NaClO_4)	25	-4.02	-6.03			66CF	P
Sm^{3+}	cal ^b	2.0 (NaClO_4)	25	-4.35	-10.06	-15.4	-20.67	64G	P
	cal ^c	2.0 (NaClO_4)	25	-3.89	-7.24			66CF	P
Tb^{3+}	cal	2.0 (NaClO_4)	25	-0.38	-3.85			66CF	P
Tm^{3+}	cal	2.0 (NaClO_4)	25	-1.21	-3.60	-7.11		66CF	P
Yb^{3+}	cal ^b	2.0 (NaClO_4)	25	-1.21	-3.21	-6.95	-2.47	64G	P
	cal ^c	2.0 (NaClO_4)	25	-1.51	-4.64	-9.46		66CF	R
Th^{4+}	cal	1.0 (NaClO_4)	25	2.09	1.26	-1.71	-5.61	78DR	P
				$\Delta H_5 = -8.00$					
UO_2^{2+}	cal	1.0 (NaClO_4)	25	5.4	12.93	12.1		78DB	P
Am^{3+}	T	2.0 (NaClO_4)	25	-5.56				72CD	P
Bk^{3+}	T	2.0 (NaClO_4)	25	-5.06				72CD	P
Cm^{3+}	T	2.0 (NaClO_4)	25	-3.89				72CD	P
2-Hydroxypropanoic acid (lactic acid)									
Be^{2+}	T	1.0 ClO_4^-	25	50.3				75TD	P
Ca^{2+}	T	0.1 (KCl)	25	45.6				75GN	P

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Table 11 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	ΔH_1	ΔH_2	ΔH_3	ΔH_4	Reference	Category
Al ³⁺	T	0.1 ClO ₄ ⁻	25	7.9				75TD	P
In ³⁺	T	0.2 (NaClO ₄)	35	13.4				73SM	P
Pb ²⁺	T	2.0 (NaClO ₄)	25	-4.2	0.0			80TG	P
Cr ³⁺	T	1.0 (ClO ₄ ⁻)	25	74.9	141.4			75TD	P
Co ²⁺	cal	1 (NaNO ₃)	25	0.08	0.62			75A	P
Ni ²⁺	cal	1.0 (NaNO ₃)	25	-0.71	-2.1			5A	P
Cu ²⁺	T	0.1 (KCl)	25	37.2	25.6			70GN	P
	cal	1.0 (NaNO ₃)	25	0.67	0.29	-0.42		75A	P
Ce ³⁺	cal ^c	2.0 (NaClO ₄)	25	-7.1	-4.6	-26.7		66CF	P
Dy ³⁺	cal	2 (NaClO ₄)	25	-9.04				66CF	P
Er ³⁺	cal ^c	2.0 (NaClO ₄)	25	-7.97	-3.8	-21.3		66CF	P
Eu ³⁺	T	1.0 (NaClO ₄)	25	-19.2	-10.0	-33.6		84LL	P
	cal	2.0 (NaClO ₄)	25	-8.1	-4.8	-23.2		66CF	P
Gd ³⁺	cal ^c	2.0 (NaClO ₄)	25	-8.24	-9.08	-20.8		66CF	P
La ³⁺	cal	2 (NaClO ₄)	25	-6.6	-11.2	-20.8		66CF	P
Nd ³⁺	cal ^c	2.0 (NaClO ₄)	25	-13.5	-7.2			66CF	P
Sm ³⁺	cal ^c	2.0 (NaClO ₄)	25	-9.75	-7.9	-38.00		66CF	P
Tb ³⁺	cal ^c	2.0 (NaClO ₄)	25	-6.9				66CF	P
Yb ³⁺	cal ^c	2.0 (NaClO ₄)	25	-9.2	-15.0	-9.2		66CF	P
Am ³⁺	T	1.0 (NaClO ₄)	25	-16.3	-2.1	-32.0		84LL	P
2-Hydroxy-2-methylpropanoic acid (a-hydroxyisobutyric acid)									
Y ³⁺	cal	2.0 (NaClO ₄)	25	-5.1	-17.3	-19.0		66CF	P
Ce ³⁺	cal	2.0 (NaClO ₄)	25	-6.2	-7.9	-31.7		66CF	P
Er ³⁺	cal	2.0 (NaClO ₄)	25	-4.1	-22.1	-15.4		66CF	P
Eu ³⁺	cal	2.0 (NaClO ₄)	25	-6.3	-13.8	-20.5		66CF	P
La ³⁺	cal	2.0 (NaClO ₄)	25	-8.2	-9.9	-24.5		66CF	P
Nd ³⁺	cal	2.0 (NaClO ₄)	25	-6.7	-13.8	-16.7		66CF	P
Tb ³⁺	cal	2.0 (NaClO ₄)	25	-6.2	-19.5	-15.4		66CF	P
Yb ³⁺	cal	2.0 (NaClO ₄)	25	-4.6	-26.4	-22.2		66CF	P
2-Hydroxy-2-phenylacetic acid (mandelic acid)									
Ca ²⁺	T	0.0	25	32.1				75DN	P
Ce ³⁺	cal	2.0 (NaClO ₄)	25	-5.3				72DC	P
Dy ³⁺	cal	0.1 (NaClO ₄)	25	-0.72	-6.1			93HY	P
	cal	2.0 (NaClO ₄)	25	-4.4				72DC	P
Er ³⁺	cal	0.1 (NaClO ₄)	25	-1.2	-9.0			93HY	P
	cal	2.0 (NaClO ₄)	25	-5.2				72DC	P
Eu ³⁺	cal	0.1 (NaClO ₄)	25	-2.0	-6.7			93HY	P
	cal	2.0 (NaClO ₄)	25	-5.8					
Gd ³⁺	cal	0.1 (NaClO ₄)	25	-1.5	-5.5			93HY	P
	cal	2.0 (NaClO ₄)	25	-4.4				72DC	P
Ho ³⁺	cal	0.1 (NaClO ₄)	25	-1.3	-5.6			93HY	P
	cal	2.0 (NaClO ₄)	25	-4.3				72DC	P
La ³⁺	cal	0.1(NaClO ₄)	25	-2.1	-2.4			93HY	P
	cal	2.0 (NaClO ₄)	25	-5.1				72DC	P
Lu ³⁺	cal	0.1 (NaClO ₄)	25	-2.2	-7.7			93HY	P
	cal	2.0 (NaClO ₄)	25	-5.1				72DC	P
Nd ³⁺	cal	0.1 (NaClO ₄)	25	-2.8	-11.7			93HY	P
	cal	2.0 (NaClO ₄)	25	-6.00				72DC	P

(continues on next page)

Table 11 (Continued).

Metal	Method	I_c/M	$t/^\circ\text{C}$	ΔH_1	ΔH_2	ΔH_3	ΔH_4	Reference	Category
Pr ³⁺	cal	0.1 (NaClO ₄)	25	-3.0	-9.2			93HY	P
	cal	2.0 (NaClO ₄)	25	-6.4				72DC	P
Sm ³⁺	cal	0.1 (NaClO ₄)	25	-2.8	-10.7			93HY	P
	cal	2.0 (NaClO ₄)	25	-6.1				72DC	P
Tb ³⁺	cal	0.1 (NaClO ₄)	25	-0.9	-2.7			93HY	P
	cal	2.0 (NaClO ₄)	25	-3.9				72DC	P
Tm ³⁺	cal	0.1 (NaClO ₄)	25	-1.5	-6.9			93HY	P
	cal	2.0 (NaClO ₄)	25	-4.8				72DC	P
Yb ³⁺	cal	0.1 (NaClO ₄)	25	-1.9	-8.1			93HY	P
	cal	2.0 (NaClO ₄)	25	-4.3				72DC	P
2-Hydroxy-2-phenylpropionic acid (atrolactic acid)									
Dy ³⁺	cal	0.1 (NaClO ₄)	25	-4.0	-13.8			93HY	P
Er ³⁺	cal	0.1 (NaClO ₄)	25	-4.7	-15.6			93HY	P
Eu ³⁺	cal	0.1 (NaClO ₄)	25	-3.6	-9.7			93HY	P
Gd ³⁺	cal	0.1 (NaClO ₄)	25	-3.4	-13.0			93HY	P
Ho ³⁺	cal	0.1 (NaClO ₄)	25	-4.4	-16.9			93HY	P
La ³⁺	cal	0.1 (NaClO ₄)	25	-2.2	-4.5			93HY	P
Lu ³⁺	cal	0.1 (NaClO ₄)	25	-5.4	-15.4			93HY	P
Nd ³⁺	cal	0.1 (NaClO ₄)	25	-3.5	-5.6			93HY	P
Pr ³⁺	cal	0.1 (NaClO ₄)	25	-3.0	-10.3			93HY	P
Sm ³⁺	cal	0.1 (NaClO ₄)	25	-3.1	-9.2			93HY	P
Tb ³⁺	cal	0.1 (NaClO ₄)	25	-3.7	-14.4			93HY	P
Tm ³⁺	cal	0.1 (NaClO ₄)	25	-4.5	-13.4			93HY	P
Yb ³⁺	cal	0.1 (NaClO ₄)	25	-5.1	-14.0			93HY	P

^aStability constants recalculated at $M = 1.0 \text{ mol dm}^{-3}$ from 70FB by Davies equation.

^b β_j from 59S.

^c β_j recalculated from the original data of 61CC.

5.2.1 2-Hydroxyacetate (glycolate) complexes

Isolated enthalpy values are available for the glycolate complexes for cerium(III), indium(III), thallium(III), and vanadyl(IV) ions. The enthalpy values of 75CSa for Tl³⁺-glycolate complexes were obtained from complexation constants determined at different temperatures. These constants have been rejected, and, therefore, the enthalpy values are also rejected. The other values are all provisional. Two papers report enthalpy changes for the formation of copper(II) complexes. The value reported in 75DN was obtained from temperature dependence of the stability constants at several different temperatures and are to be considered as provisional. The calorimetric value of 75A has also been evaluated as provisional. The temperature variation result of 84II for scandium(III) complexes has been rejected, because the reported value has been determined for the stability constant determined at only two temperatures (25 and 40 °C), and because the enthalpy value thus obtained ($\Delta H = 121 \text{ kJ mol}^{-1}$) is abnormally high.

The two calorimetric results for yttrium(III) complexes, from different research groups, are in reasonable agreement as far as ΔH_1 and ΔH_2 are concerned, and are, therefore, regarded as provisional. On the contrary, the agreement between the ΔH_3 values in the two papers is not so satisfactory, but in one case [66CF], the assumption is that three ligands are coordinated to the metal ion and in the other case [64G], the number of ligands coordinated to yttrium(III) is assumed to be four. It is not casual perhaps that the ΔH_3 value of 66CF is almost equal to the sum of ΔH_3 and ΔH_4 of 64G. Several data are available on the complexation enthalpy of glycolate with lanthanides(III), obtained both from temperature

dependence of equilibrium constants and calorimetry. When the agreement among the enthalpy values obtained by the two methods is not satisfactory, the enthalpy values determined by temperature variation method have been rejected to emphasize the lower accuracy and precision of this method. This is the case of temperature variation values of 61CC for cerium(III) and gadolinium(III) complexes and of 72CD for europium(III) complexes. The enthalpy changes of europium(III) complexes of 68L, calculated from complexation constants measured at several different temperatures, were rejected. Thus, the corresponding enthalpy changes are rejected, too. The calorimetric results of 64G and 66CF for the glycolate complexes of gadolinium(III) and ytterbium(III) show excellent agreement and are, therefore, recommended.

The remaining enthalpy values have been considered as provisional.

5.2.2 2-Hydroxypropanoate (lactate) complexes

A relatively smaller number of reports are available on the enthalpy changes of metal ion complexation with lactate ion. The data concerning the enthalpy values of complexation of the main group elements and transition-metal ions are provisional, except the data reported by 69RB, which are rejected because the stability constants by which these values were calculated were rejected. The calorimetric values of 78FB must also be rejected in view of the formation of lead(II) and copper(II) complexes claimed by the authors (see Section 5.1).

Most of the data concerning the complexation of lanthanide(III) ions are from the same group [61CC, 66CF]. The enthalpy changes were obtained by the temperature variation method [61CC] and by calorimetry [66CF]. The data calculated from the stability constants are in considerable disagreement with those calculated by calorimetry and have been not accepted [71ALa, 78FB].

5.2.3 2-Hydroxy-2-methylpropanoate (α -hydroxyisobutyrate) complexes

For this ligand, too, the enthalpy data are available only for a few elements. The temperature variation result for scandium(III) complex is rejected for the reason given above for complexes of this ion with glycolate and mandelate [84II]. The remaining values are from the same research group. The enthalpy changes calculated by the temperature variation method are always lower than those obtained calorimetrically. The latter have been evaluated as provisional, and the former are rejected [61CC].

5.2.4 2-Hydroxy-2-phenylacetate (mandelate) complexes

Only four papers report enthalpy changes for complexation of metal ions with mandelate ion. The temperature variation result of 75DN for calcium(II) complex is provisional. This method has also been used for calculating the enthalpy changes accompanying the formation of scandium(III) complex. This value is based on the determination of stability constants at two temperatures only (25 and 40 °C) and, therefore, it is rejected [84II]. Two papers [72DC, 93HY] report enthalpy changes of the mandelate complexes of lanthanide(III) ions at different ionic strengths. These values are provisional. The temperature variation method was used to determine the enthalpy change for praseodymium(III) complexation. The resulting values are rejected because they are much higher than what would be expected on the basis of the other values [82KM].

5.2.5 2-Hydroxy-2-phenylpropanoate (atrolactate) complexes

Only one paper [93HY] reported enthalpy values for the complexation of this ligand with lanthanides(III). The values are all considered provisional.

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