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CRITICAL EVALUATION OF STABILITY CONSTANTS OF METAL-IMIDAZOLE AND METAL-HISTAMINE SYSTEMS**

(Technical Report)

Prepared for publication by
STAFFAN SJÖBERG
Department of Inorganic Chemistry, Umeå University, S-90187 Umeå, Sweden

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

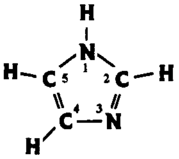
Critical survey of stability constants of metal–imidazole and metal–histamine systems (Technical Report)

Abstract: Thermodynamic data for the proton and metal ion complexation equilibria of imidazole (1,3 - diazole, glyoxaline) and histamine (4-imidoazolethylamine, 4 - (2′ - aminoethyl) imidazole) have been collected and critically evaluated. The literature search has been performed by using IUPAC's "Stability Constants Database" and covers the literature until 1992. Important criteria for acceptance comprise specification of the essential reaction conditions, the correctness of calibration techniques and appropriate equilibrium analysis of experimental data. Recommended values with respect to proton - ligand and metal ion - ligand equilibria have been tabulated. Furthermore, the medium dependence of these reactions has been evaluated using an extended Debye - Hückel expression.

INTRODUCTION

The imidazole moiety is a versatile binding site in different biological systems. It functions as a binding site in iron-heme systems, vitamin B_{12} and its derivatives and in several metalloproteins, e. g. carbonic anhydrase, carboxypeptidase A and bovine superoxide dismutase.

The name imidazole (1,3- diazole) is due to Hantzsch (1888HA), who classified as azoles the five - membered polyheteroatomic ring systems containing at least one tertiary nitrogen. The term imidazole implies a five-membered, heterocyclic ring system containing, in addition to a tertiary nitrogen, an imino group. Similarly, the names oxazole and thiazole designate five- membered ring systems containing in addition to the tertiary nitrogen an oxygen or sulphur atom.



The imidazole ring is aromatic and consequently planar. Its structural features are discussed with reference to pyridine and pyrrole, to both of which imidazole is structurally related. The N-3 nitrogen of imidazole is frequently termed the pyridine nitrogen, while the N-1 nitrogen is called the pyrrole nitrogen.

The electron pair on N-3 is the only one properly described as an unshared pair. The π electrons of N-1 are part of the aromatic sextet. This implies that bonding of a proton or a metal ion at N-1 is expected to be unfavourable since the aromaticity of the ring is thereby disturbed. To conclude, the energetically most likely coordination site for a proton or a metal ion is the unshared pair on N-3 of the neutral imidazole molecule.

In the protonated imidazolium cation the N-1 and N-3 nitrogens are equivalent, which is evident from the appearance of a single peak in its ^1H n.m.r. spectrum.

In addition to its basic nature, imidazole also exhibits weakly acidic properties. The neutral imidazole deprotonates at N-1 in strongly basic solutions with reported pKa value ≥ 13 (see below). The resulting anionic imidazole, imidazolate, exhibits two equivalent sites for coordination and can act as a bridging ligand.

The stability of metal - imidazole complexes is in agreement with the Irving - Williams sequence, i.e., Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). Furthermore, the stability constants of imidazole complexes with these transition metals are greater than the corresponding ones for pyridine and ammonia. In the case of pyridine, this can be explained by the higher basicity of imidazole. Though the basicity of ammonia is almost two logarithmic units higher than imidazole, the latter forms slightly stronger complexes with 3d metal ions. This can be ascribed at least partly to its greater π acceptor properties, which permit it to accept electronic charge from d orbitals on the metal ion.

Besides imidazole, a great number of imidazole derivatives have been studied. However, except for histamine and histidine the number of published stability constants are too few to allow a rigid evaluation. As histidine has been evaluated within the group of amino acids (84PEa), it is not considered in this study.

The present study attempts to evaluate reported thermodynamic data (stability constants, enthalpy values) for proton and metal ion binding constants of imidazole and histamine (4-imidoazolethylamine) in aqueous solution. The aim is also to recommend a reasonable and internally consistent set of values for use in quantitative assessment of their chemical and biochemical reactions.

METHOD OF EVALUATION

Data have been evaluated and grouped into four categories: recommended (R), tentative (T), doubtful (D) and rejected (Rj).

For acceptance the following criteria are regarded as important in the evaluation and the appropriate information should therefore appear in the paper:

(i) The purity of reagents and solvents, and the procedures for purification.

(ii) The temperature, composition of ionic medium and ionic strength.

(iii) Metal and ligand concentrations as well as ligand to metal ratios.

(iv) The instruments used and an explicit description of the method of calibration.

When a pH-electrode is used it should be stated whether the activity or the concentration of H^+ is applied.

(vi) Results from reproducibility and reversibility tests and the number of data points in different data sets.

(vii) Unambiguous definition of the equilibrium constants reported.

(viii) Details of the equilibrium analysis - graphical and/or computerised methods

(ix) An unbiased search for the speciation scheme, i. e., a model should be fitted to the experimental data - not the opposite.

(x) A visual presentation of the fit of the model to the experimental data.

On the basis of these criteria data were grouped into the four different categories according to the guidelines put forward by IUPAC in 1975 (75CE). The data which passed the above-mentioned acceptance criteria were averaged, and depending on the standard deviation (s.d.) of the average values, were regarded as recommended (s.d.$\leq$ 0.05 log units) or tentative (0.05 < s.d. $\leq$ 0.2 log units).

A critical evaluation of the stability constants is most easily accomplished by comparing literature values which were determined under identical conditions of temperature and ionic strength. (If data from different research groups are in close agreement the constant is regarded as well substantiated.) A variety of temperatures (0–50 °C) , ionic strengths (0.058–5.0 M; M ≡ mol dm^{-3}) as well as composition of background electrolytes (e. g., KNO_3, $NaNO_3$, $NaClO_4$, NaCl, KCl, K_2SO_4)has been utilised. Consequently, it has been necessary to adjust the constants to those under the same conditions for comparison.

The temperature adjustment to 25°C was made using recommended enthalpy values and the van't Hoff relationship:

$$d(\log K)/dT = \Delta H^0 / 2.303\,RT^2 \qquad (1)$$

If it is assumed that the temperature dependence of ΔH^0 is negligible (which often is a fair approximation within the limited temperature range (20–37 °C) discussed in the present paper), these enthalpy values may be used to estimate log K values at other temperatures. Integration of equation (1) then gives:

$$\log K_{T2} = \log K_{T1} + \Delta H^0 (T_2 - T_1)/2.303\,R\,T_1\,T_2 \qquad (2)$$

In this way internal consistency between values determined at different temperatures could be checked.

Useful interpolating equations for estimating stability constants at different ionic strengths include the following:

$$\log K_n = \log K_n^0 + A\Delta Z^2 I^{1/2}/(1+BI^{1/2}) + CI + DI^{1/4} \quad (3)$$

where $K_n{}^0$ is the extrapolated constant to the infinite dilution standard state. A is a function of the absolute temperature and the electric permittivity for the solvent and ΔZ^2 is the difference between the sum of squared product ion charges and reactant charges. I is the ionic strength and B, C and D are constants appropriate to a given equilibrium. As $\Delta Z^2 = 0$ with respect to K_1 of imidazole and histamine, as well as for the formation of binary metal - imidazole and metal histamine complexes, the Debye-Hückel term equals zero. By plotting the corresponding constants versus the ionic strength, linear relationships were established. By comparing different data sets consistency with respect to the extrapolated $K_n{}^0$ -value corresponding to different medium compositions (e. g., KNO_3, $NaClO_4$, NaCl) could be checked.

The majority of the reported stability constants are based upon the potentiometric titration technique using a glass electrode and in some cases also amalgam or ion selective electrodes. The constant ionic medium method has been utilised with ionic strengths mostly ranging from 0.1 to 3.0 M. As a "rule of thumb" not more than 10 % of the medium ions should be exchanged for reacting species, otherwise changes in activity coefficients will become significant during a titration. Depending on the medium a limit is thus set with respect to the upper concentration of the metal and the ligand which can be used such that the activity coefficients will be kept constant. Furthermore, stepwise stability constants are frequently determined from ñ (log[L])-graphs , where ñ is the average number of ligands bound per metal ion given by the relation:

$$\tilde{n} = ([L]_{tot} - [L] - [HL^+]) / [M]_{tot} \quad (4)$$

At high ligand to metal ratios and with $pH>pK_a$, conditions necessary to determine composition and stability of higher species within the series ML_n, the dominator in this equation tends to become the difference between two large numbers, giving rise to uncertainties in ñ. This implies that small errors in the total ligand concentration and/or an error in the protonation constant of the ligand will cause great uncertainties in ñ.

As a consequence of these experimental difficulties, the evaluation of log $K \leq 1.0$ are associated with great uncertainties if the ionic strength is kept at values 0.15 or less. In the present evaluation, such constants are regarded as doubtful. This situation arose when determining K_5 and K_6 for some of the 3d metal ion systems.

REPORTED VALUES

Throughout this evaluation, stability constants and enthalpy values are given for both proton and metal ion complexes of imidazole and histamine.

When a concentration scale for H^+ was applied the corresponding constants are referred to as "concentration" constants (C) in contrast to "mixed" constants (M) in which an activity scale of H^+ was utilised. In the evaluation of the medium dependence of the protonation constant of imidazole, mixed constants valid at I=0.1 M were recalculated to concentration constants by using an activity coefficient of 0.78 for H^+, which decreases the constants by 0.11 units. No distinction is made in this survey between concentration and mixed constants for the metal complexes of imidazoles.

In the literature search IUPAC's Stability Constants Database (93PP) supplemented with the book volumes of Stability Constants (64SM, 71SM) were used. The search covers the literature up to 1992. For a complete listing of the data the reader is referred to these sources.

The amphoteric properties of imidazole (L), giving rise to the imidazolium cation (HL^+) and the imidazolate ($H_{-1}L^-$) anion, are characterised by the following equilibria:

$H^+ + L = HL^+$ (protonation of the N-3 nitrogen)

$-H^+ + L = H_{-1}L^-$ (deprotonation of the N-1 nitrogen)

The constants K_1 and K_{-1} are assigned to the corresponding reactions.

For the formation of a series of mononuclear complexes ML_n, the following equilibria

$ML_{n-1} + L = ML_n$

with corresponding stepwise stability constants, K_1 - K_n, are discussed. In some cases overall constants β_1 - β_n are used, especially when some intermediate β - values were found missing.

Due to the higher basicity of the α-amino group of the side chain in histamine, K_1 reflects the affinity for protonation of this group, whereas K_2 is ascribed to the protonation of the N-3 nitrogen of the imidazole ring.

Histamine contains three functional groups: a) the α-amino group, b) the secondary imidazole nitrogen, and c) the tertiary imidazole nitrogen. However, it has been shown that the secondary nitrogen atom does not take part in the coordination reaction. Histamine therefore acts as a bidentate ligand.

Table 1.1. Enthalpy values for the formation of imidazolium (HL^+, $\Delta H^0(K_1)$) and imidazolate ($H_{-1}L^-$, $\Delta H^0(K_{-1})$ as well as for different metal complexes of imidazole. All values are in kJ mol^{-1}. t denotes values obtained from the temperature dependence of the stability constants and cal denotes calorimetrically determined values.

I/M^{z+}	Medium	$\Delta H^0(K_1)$	$\Delta H^0(K_2)$	$\Delta H^0(K_3)$	$\Delta H^0(K_4)$	Ref.	Rem.	Cat.
H^+								
0-corr.		-36.8				66DGb	t	T
0.15	$NaNO_3$	-31.4				53TW	t	Rj
0.16	$NaClO_4$	-35.9				88ABc	t	T
0.20		-36.78				62WA	cal	T
0.50		-38.1				78MHa	cal	T
0.15	NaCl	-35.6				88ABc	t	T
0.10	KNO_3	-38				86TVa	t	T
0.16		-38.1				64BWa	cal	T
0.10	KNO_3	38$^{1)}$				86TVa	t	Rj
0-corr		73.6$^{1)}$				64GHf	t	D
Co^{2+}								
0.16	KNO_3	-17.6	-16.3	-14.6	-16.5	66SKf	t	D
0-corr		-20.5				74LVa	t	D
Ni^{2+}								
0.16	KNO_3	-21.8	-19.3	-18.0	-16.5	66SKf	t	D
0-corr		-28.7	-6.3			74LVa	t	D
0.16	KNO_3	-24.3				64BWa	cal	T
Cu^{2+}								
0.16	KNO_3	-30.2	-22.7	-19.3	-12.6	66SKf	t	D
0-corr		-28.6	-34.4	-60	35	74LVa	t	D
0.16	KNO_3	-31.8				64BWa	cal	T
Zn^{2+}								
0-corr		-12.8				74LVa	t	D
0.16	KNO_3	-15.9				64BWa	cal	T
Cd^{2+}								
0-corr		-26.8	-31.2			74LVa	t	D
0.5	$NaClO_4$	-20.4	-20.3			78MHa	cal	T
Hg^{2+}								
0.5	$NaClO_4$	-75	-32.1			78MHa	cal	T
Ag^+								
0.1	KNO_3	-24	-40			66DGb	t	D
1.0	KNO_3	-30.5	-35.1			64BWa	cal	T
Hf^{4+}								
0.5	$NaClO_4$	-33.27				76EWa	cal	T

1) $\Delta H^0(K_{-1})$

PROTON COMPLEXATION CONSTANTS

Protonation enthalpies

Imidazole. The accuracy of enthalpy values determined calorimetrically is usually greater than those obtained from the temperature dependence of stability constants. Hence the calorimetric studies by 78MHa and62WA giving $\Delta H^0(K_1) = -38.10(12)$ kJ mol^{-1} (I=0.5 M $NaClO_4$, 25 °C), and $\Delta H^0(K_1) = -36.78(17)$ kJ mol^{-1} (I=0.20 M $NaClO_4$, 25 °C), respectively are regarded as the most reliable ones (T). A linear extrapolation of these two values gives $\Delta H^0(K_1)$=-35.9 kJ mol^{-1} at I=0 and 25 °C. This value is somewhat smaller than that reported by 66DGb, who obtained a value of -36.8 kJ mol^{-1} (potentiometric titration data). The value presented by 53TW is obviously wrong and is rejected. There is a good agreement between values from KNO_3-media. However, these values are about 2 kJ mol^{-1} lower than the data from NaCl and $NaNO_3$ media (cf. Table 1.1). To what extent this difference is a medium effect or not is difficult to tell from available data.The characterisation of thermodynamic quantities for the deprotonation of imidazole to yield the imidazolate ion is met with difficulties. Imidazole is a very weak acid (pK_a approx. 14.5, see below) and only two $\Delta H^0(L=H_{-1}L^- + H^+)$ values are reported (c.f. Table 1.1). George et al. (64GHf) have reported a value of 17.6 kcal mol^{-1} (73.6 kJ mol^{-1}) based upon spectrophotometric measurements at three different temperatures (15.3–35.3 °C). To obtain this value (valid at I=0) they used an empirical relationship in which the ionic strength dependence was corrected from 0.5 M KNO_3 medium simply by including the term 0.10 $I^{1/2}$. Considering this approximation the value has to be regarded as doubtful. The value reported by 86TVa (38 kJ mol^{-1}) is based upon potentiometric titrations (glass electrode) at different temperatures. This value is rejected due to the very low accuracy of this method in such alkaline solutions.

Histamine The enthalpy changes accompanying the protonation of histamine are listed in Table 1.2. The results were obtained from both calorimetric and potentiometric titrations at different temperatures. The results published by 60NF are based on titrations within a narrow temperature range and are regarded as uncertain. As the values are significantly higher than the other they were not included in the critical evaluation. Values reported by Gergely and Sovago in 73GSb were later (76GS) redetermined with values in better agreement with other studies (70MBb, 79MBb) of the same ionic strength.

Recommended and tentative protonation enthalpies of imidazole and histamine are given in Table 2.

Table 1.2 Enthalpy values for the protonation of histamine and for metal histamine complexes. All values are in kJ mol^{-1}.

I	Medium	$\Delta H^0(K_1)$	$\Delta H^0(K_2)$	$\Delta H^0(\beta(\mathrm{MHL}))$	Ref.	Rem.	Cat.
H^+							
0-corr		-56.1	-42.3		60NF	t	D
0.1	KNO_3	-50.8	-31.4		84ACb	cal	R
0.1		-50.0	-31.7		70EH	cal	R
0.16		-52.50	-31.0		70MBb	cal	T
0.2		-52.7	-32.2		79MBb	t	R
0.2	KCl	-53.2	-32.3		76GS	cal	R
0.2		-54.4	-35.6		73GSb	cal	T
Mn^{2+}							
0.2	KNO_3	-2.1	-2.1		71RMd	t	D
Co^{2+}							
0-corr		-28.9	-20.1		60NF	t	D
0.2	KNO_3	-18.4	-19.2		71RMd	t	D
Ni^{2+}							
0-corr		-45.6	-34.3		60NF	t	D
0.2	KNO_3	-26.4	-27.6		71RMd	t	D
0.3	$NaClO_4$	-32.5	-29.3	-25.3$^{4)}$	67HW	cal	T
0.2	KCl	-42.7	-36.8		76GS	cal	T

Cu^{2+}							
0-corr		-64.9	-48.5		60NF	t	D
0.01	?	-33.5	-25.1		62HJa	t	D
0.1	KNO_3	-50.6	-42.4	-74.8	84ACb	cal$^{1)}$	T
0.1		-47.7	-40.1		70EH	cal	T
0.16		-56.4	-45.4		70MBb	cal	D
0.2		-51.5	-41		79MBb	t	T
0.2		-45.9	-42.7		71RMd	t	D
0.2	KCl	-54.3	-41.1		76GS	cal$^{3)}$	T
0.3	$NaClO_4$	-43.1	-42.0		67HW	cal	T
Zn^{2+}							
0.1	KNO_3	-23.9	-19.6	-60.6	84ACb	cal	T
0.2		-16.7	-15.5		71RMd	t	D
Cd^{2+}							
0.1	KNO_3	-26.8	-24.4	-71.1	81AAc	cal$^{2)}$	T

1) $\Delta H^0(\beta(CuHL_2)$ = -121 kJ mol^{-1}. 2) $\Delta H^0(K_3)$ = 0.2 kJ mol^{-1}. 3)$\Delta H^0(\beta(CuHL_2))$=-129.0 kJ mol^{-1}. 4) $\Delta H^0(K_3)$.

Table 2. Recommended and Tentative Protonation Enthalpies (kJ mol^{-1}) of Imidazole and Histamine at 25 °C.

Ligand	I	$\Delta H^0(K_1)$	$\Delta H^0(K_2)$	Cat.
Imidazole	0	-35.9(2)		T
	0.2	-36.8(2)		T
	0.5	-38.1(2)		T
Histamine	0.1	-50.4(4)	-31.6(2)	R
	0.2	-52.8(3)	-32.2(1)	R

Protonation constants

Imidazole The assumption of a linear relationship between log K_1 and ionic strength (I) was assumed for each of the different ionic media studied. Linear regression analyses (log K = log K^0 + CI; c.f. eq. (3)) were performed using, besides the value by 66DGb, the reported concentration constants in KNO_3 (I = 0–1.0 M), $NaClO_4$ (I = 0–4.0 M) and NaCl (I = 0–5.0 M) media (cf. Table 3.1).

Table 3.1. Protonation constants of imidazole. Some values have been recalculated to 25 °C using enthalpy values from Table 2.

I	Medium	log K_1	Constant	Ref.	Cat
0 corr		6.993	A	66DGb	R
0.1	KNO_3	7.002	C	86TVa	R
0.2		7.12	M	63CCb	T
0.5		7.14	M	89BLa	T
0.5		7.18	M	86BGa	T
0.5		7.22	M	83LWa	T
1.0		7.33	C	69NNa	R
	$NaNO_3$				
0.1		7.04	C	81BKb	R
0.1		7.04	M	82SSa	D
0.16		7.06 (7.11)$^{1)}$	M?	54EF	D
0.15		7.12	M?	53TW	D
	$NaClO_4$				
0.15		7.11(7.20)$^{2)}$	M	62HJa	T
0.15		7.20(6.95)$^{3)}$	M	80NSb	T
0.15		7.12(7.06)$^{4)}$	?	60BD	T

0.16		7.075	C	88ABc	R
0.16		6.68	?	78SPc	Rj
0.5		7.20	C	78MHa	R
3.0		7.913	C	72SJa	R
0.25		7.05	C	69LVa	R
0.5		7.13	C		R
1.0		7.29	C		R
2.0		7.58	C		R
4.0		8.18	C		R
	NaCl				
0.15		7.077	C	88ABc	R
1.0		7.215	C	79FOa	R
3.0		7.637	C	71SJa	R
5.0		8.12	C	73SJa	R
	KCl				
0.1		7.09	?	64BWa	T
0.135		7.09	?	55MA	T
0.058		7.06	?	61SM	T
0.3	K_2SO_4	7.01	M	61JWa	D

1) 22.5 °C 2) 20 °C 3) 37 °C 4) 27 °C

The analysis indicated a very good fit for these data. This also simplified the problem of identifying less reliable data. The calculations resulted in $logK^0$ - values 6.99, 7.01 and 7.01 respectively, with the value 7.01 representing the recommended value. A compilation of the results obtained is given in Table 4.

It may thus be concluded that an evaluation of existing K_1 values has allowed for the determination of not only a value of log K_1^0 =7.01, but also for the medium and ionic strength dependence in concentrated electrolyte solutions (I as high as 5.0 M).

Deprotonation of the imidazole molecule to yield the imidazolate ion has been observed in strongly alkaline solutions. 86TVa reported log K_{-1} = -12.588 from glass electrode measurements in 0.1 M KNO_3 medium. As the potentiometric titration technique cannot be regarded as sensitive enough in such alkaline solutions (especially when using a glass electrode) to provide accurate experimental data, this value is rejected. This value also deviates strongly from -14.44 (64GHf), and -14.52 (56WI) based on spectrophotometric measurements. These latter values are regarded as tentative and no recommended value can be given due to a too limited data set.

Histamine The main part of the protonation constants for histamine have been performed within the range $0.1 \le I \le 0.2$ M (Table 3.2). This range is too limited to allow for a determination of the ionic strength dependence of K_1 and K_2 as was done for imidazole. Instead recommended and tentative values will be given for I=0.1 and 0.2 M.

In the evaluation, studies by 64ARb and 71RMd were excluded because the experimental conditions were not satisfactory specified. Furthermore, the ligand concentrations studied by 85RRc were too low to permit an accurate determination of K_1 and this value is regarded as doubtful. The values by 76DOb, 85DRc and 80GMb are in excellent agreement and are recommended. There is also good agreement in reported values at I = 0.2 M (79MBb, 63CCb,73GSb). This evaluation is based on values for the different concentration constants. A recalculation of presented mixed constants to concentration constants shows upon an acceptable agreement with $I \le 0.1$ M.

Recommended and tentative protonation constants for imidazole and histamine are found in Table 4.

METAL COMPLEXATION CONSTANTS

Metal complexation enthalpies

Metal Imidazoles Reported enthalpy values for the different metal - imidazole complexes are scarce (cf. Tables 1.1). The reported values by 74LVa are based upon the temperature dependence of the different β^0_n values obtained from potentiometric titration at 15, 25, and 35 °C. As the major part of these β values was regarded as doubtful (see below), the evaluated ΔH^0 values must be associated with great uncertainties as well. Due to the poor agreement between the values by 66SKf and the corresponding values obtained from calorimetric measurements, the former were regarded as doubtful as well. What remains then are tentative $\Delta H_n{}^0$ values for Ni^{2+} (n=1), Cu^{2+} (n= 1), Zn^{2+} (n=1), Cd^{2+} (n=1,2), Hg^{2+} (n=1,2), Ag^+ (n=1,2) and Hf^{4+} (n=1). These values are presented in Table 5.

Table 3.2 Protonation constants of histamine. Some values have been recalculated to 25 °C using enthalpy values from Table 2.

I	Medium	log K_1	log K_2	log β_2	Const.	Ref.	Cat.
0.1	KNO_3	9.81	6.08	15.89	C	76Dob	R
		9.79	6.07	15.86	C	80GMb	R
		9.92	6.05	15.97	C	85RRc	T
		(9.63)1)	(5.87)1)	(15.50)1)			
		9.88	6.13	16.01	?	64Arb	T
0.15		9.92	6.22	16.14	M	67PSc	T
		(9.57)2)	(6.01)2)	(15.58)2)			
0.16		9.97	6.25	16.22	M?	70MBb	D
0.2		9.93	6.20	16.13	?	71RMd	T
		9.88	6.16	16.04	C	79MBb	R
		9.87	6.2	16.07	M	63CCb	T
0.5		9.52	6.48	16.00	M	83LWa	D
0.058	KCl	9.87	6.14	16.01	M	61SM	
0.1		9.70	6.02	15.72	C	64Dca	T
		9.83	6.07	15.90	C	85DRc	R
0.12		9.88	6.12	16.00	M	70Caa	T
0.135		9.88	6.13	16.01	M	55MA	T
0.2		9.85	6.16	16.01	C	73GSb	R
0.1	$NaClO_4$		6.13		C	77STb	T
0.15		9.74	6.16	15.90	C	80NSb	D
		(9.39)2)	(5.95)2)	(15.34)2)			
0.2		9.93	6.34	16.27		84PBd	D

1) 35 °C. 2) 37 °C.

Table 4. Recommended and tentative values (25°C) for the protonation constants of imidazole and histamine . The estimated errors of the logarithms of the recommended constants are ±0.02. C is defined according to equation 3.

	Log Kn	I = 0	I = 0.1	I = 0.5	I = 1.0	I = 3.0	C	Cat.
				Imidazole				
H^+	log K_1	7.01	7.04	7.18	7.34		0.33	R1)
	"	7.01	7.04	7.18	7.34		0.33	T2)
	"	7.01	7.04	7.17	7.31	7.89	0.30	R3)
	"	7.01	7.03	7.11	7.22	7.64	0.21	R4)
	"	7.01	7.03	7.11	7.22	7.64	0.21	T5)
			I= 0.1	I= 0.2				
				Histamine				

H^+	$\log K1$	9.81	9.86	R
	$\log K_2$	6.07	6.13	R

1) KNO_3 2) $NaNO_3$ 3) $NaClO_4$ 4) NaCl 5) KCl media.

Table 5. Tentative enthalpy changes (kJ mol^{-1}) for the formation of metal complexes with Imidazole and Histamine respectively at 25 °C

Ligand	M^{z+}	I	$\Delta H^0(K_1)$	$\Delta H^0(K_2)$	$\Delta H^0(\beta(MHL))$	Cat.
Imidazole						
	Ni^{2+}	0.16	-24.3			T
	Cu^{2+}	0.16	-31.8			T
	Zn^{2+}	0.16	-15.9			T
	Cd^{2+}	0.5	-20.4	-20.3		T
	Hg^{2+}	0.5	-75.0	-32.1		T
	Ag^+	0.5	-30.5	-35.1		T
	Hf^{4+}	0.5	-33.3			T
Histamine						
	Ni^{2+}	0.2–0.3	-37.6(5.0)	-33.1(3.7)	-25.3 1)	T
	Cu^{2+}	0.1–0.3	-51.0(2.0)	-41.3(1.0)	-74.8	T
					-125 2)	T
	Zn^{2+}	0.1	-23.9	-19.6	-60.6	T
	Cd^{2+}	0.1	-26.8	-24.4	-71.1	T

1) $\Delta H^0(K_3)$; 2) $\Delta H^0(\beta(MHL_2))$

Metal Histamines Enthalpy values are reported with respect to the metal ions Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) (cf. Table 1.2). The values reported by 60NF, 62HJa and 71RMd were not regarded as reliable because of low accuracy in reported stability constants and narrow temperature ranges of the corresponding titrations (10–40 °C, (60NF); 0, 25 °C, (62HJa); 15, 25, and 40 °C, (71RMd)). Values for Ni(II)-histamine complexes (calorimetric measurements) are presented by 67HW and 76GS. There is a significant discrepancy between the reported values. Reasons for this are difficult to find, hence both sets of constants are regarded as tentative.

In the Cu(II)-system values reported by 84ACb are regarded as the most reliable. In this study protonated ($CuHL^{3+}$,$CuHL_2^{3+}$) and deprotonated ($CuH_{-1}L^+$, $Cu_2H_{-2}L_2^{2+}$) species were accounted for in the data evaluation. The formation of these species were neglected in the other studies, which (dependent on the experimental conditions) will introduce uncertainties in measurements at low ligand to metal ratios. This may be the reason why there is quite a significant spread in reported $\Delta H^0(K_1)$ - values, while the agreement in $\Delta H^0(K_2)$ is good.

The careful studies performed by Arena et al. of the Zn(II) system (84ACb) and Cd(II) system (81AAc) resulted in enthalpy values which are regarded as tentative as long as no comparable work is available.

Tentative values of the different metal - histamine systems are found in Table 5.

Metal Complexation Stability Constants.

Metal Imidazoles Of the different metal systems, those for the 3d transition metal ions have been studied in most detail. However, data are only found for Mn(II), Fe(II), Co(II), Ni(II), Cu(I), Cu(II) and Zn(II).

Within the 4d and 5d series, data are reported for Ag(I), Cd(II), Pd(II) and Hg(II). In addition imidazole complexation to Pb(II) and Hf(IV) have been studied. A compilation of published values is given in Table 6.

A common feature of metal complexation to imidazole and its derivatives is the stepwise formation of a series of mononuclear complexes ML_n^{z+}. In solutions with ligand to metal ratios less than four, the formation of mono- or polynuclear mixed hydroxo-imidazole complexes have been postulated (71SJa, 72SJa, 73SJa, 83ERa, 79FOa, 75FSa, 77FOa, 79GSb, 81GSa, 78MHa, 77SJc). It has also been demonstrated that in ionic media containing chloride ions ternary metal - chloro - imidazole complexes are formed (77SJa (Cu), 78FOa (Ni), 77FOb (Zn), 77SJc (Hg), 81FGa (Co), 83GSa (Cd)).

Table 6. Stability constants (logarithmic values) of metal imidazole complexes. A * denotes that the corresponding constant is not included in the evaluation of recommended values. The temperature is 25 °C unless otherwise stated.

I	Medium	K_1	K_2	K_3	K_4	K_5	K_6	Ref	Rem
Mn^{2+}									
0.16	KNO_3	1.25	0.70					66SKf	30 °C
0.16	?	1.65*	1.25*					58ME	
0.10	$NaNO_3$	1.25						82SSa	
0.5	KNO_3	1.32	0.98	0.93*				89BLa	
Fe^{2+}									
0.16	KNO_3	1.81	1.23					66SKf	30 °C
0.058	KCl	3.20*	3.17*					61SM	
Co^{2+}									
0.16	KNO_3	2.47	1.93	1.45	1.00	0.5*	0*	66SKf	
0.16	?	2.42	1.95	1.58	1.2			58ME	
0.15	?	2.23*						58SL	
0.15	$NaNO_3$	3.02*	2.58*					83ERa	37 °C
0.50	KNO_3	2.70	2.08	1.36*	1.49*	0.08*		83LWa	
0.10	$NaNO_3$	2.40						82SSa	
0.5	$NaClO_4$	2.484		β_3=	6.52*			74LVa	
0.25		2.476	β_3=	6.66*					
1.00		2.511	β_3=	6.87*					
2.00		2.525		β_4=	8.69*				
3.0	"	2.73	2.18	1.61	0.92			81FGa	
0.1	"	2.43						68ISa	
0.5	NH_4NO_3	2.23	1.86*	0.91*	1.01*	0.70*	0.57*	71BLb	
Ni^{2+}									
0.2	KNO_3	3.01						63CCb	
0.15	"	3.27	2.68	2.15	1.65	1.12*	0.52*	55LCa	
0.16	"	3.09	2.47	2.00	1.54	1.1*	0.5*	66SKf	
0.5	"	3.16	2.60	2.00	1.40			83LWa	
0.135	KCl	2.94	2.41	1.99	1.3			55MEa	
0.15	$NaNO_3$	3.198	2.05*	β_4=	10.1*			83ERa	37 °C
0.10	"	3.03						82SSa	
0.16	$NaClO_4$	3.20						78SPc	
0.10	"	2.94						68ISa	
3.00	"	3.344	2.743	2.22	1.61			75FSa	
0.50	"	3.034	2.49*		β_5=	12.3*		74LVa	
0.25		2.993	2.57*						
1.00		3.105	2.443	2.16*	2.33*				
2.00		3.238	2.40*	2.41*	2.43*				
4.00		3.454							
0.50	NH_4NO_3	3.02	2.43	2.05	1.6	1.1*	0.5*	71BLb	
Cu^{+}									
0.2	KNO_3	β_2=	11.1					72CMd	

0.3	K_2SO_4	β_2=	10.44					61JWa	
0.15	KNO_3	β_2=	10.8					54LCa	
0.15	Na_2SO_4	5.78	5.2					62HPa	
Cu^{2+}									
0.16	KNO_3	4.31	3.53	2.92	2.14			66SKf	
0.2		4.15	3.52					63CCb	
0.15				β_4=	12.6*			54LC	
0.2		4.11	3.33					89PVa	35 °C
0.5		4.30	3.55	3.07	2.17	0.65		83LWa	
0.16	$NaNO_3$	4.36	3.57	2.85	2.00			54EF	22.5 °C
0.10		4.21						82SSa	
0.15		4.015*	3.53*	2.52*				83ERa	37 °C
0.10	$NaClO_4$	4.20						68ISa	
0.15		4.21	3.34	3.18	2.18			80NSb	37 °C
0.15		4.26	3.61	2.86	2.25			62HJa	
0.25		4.17*	3.65*	2.73*	3.48*			74LVa	
0.50		4.228	3.55	2.95*	3.22*				
1.00		4.267	3.69*	β_4=	14.11*				
2.00		4.483	3.621	3.53*	-				
3.0		4.66	3.98	3.30	2.66			71SJa	
3.0		4.66	3.98	3.30	2.66	1.0	0.4	72SJa	
0.3	K_2SO_4	4.33*	3.27*	2.7*	1.9*			61JWa	
0.135	KCl	4.20	3.47	2.84	2.0			55MA	
0.16	?	4.33	3.54	2.82	2.03			57NG	
Zn^{2+}									
0.2	KNO_3	2.13*						63CCb	
0.5	“	2.70	2.55	2.23	2.0	1.52*		83LWa	
0.16	$NaNO_3$	2.58	2.37	2.23	2.02			54EF	24 °C
0.16	?	2.57	2.36	2.22	2.01			57NG	
0.16	?	2.52	2.32	2.32	2.05			58KK	
0.15	?	2.6						58SL	
0.058	KCl	3.15	2.95					61SM	
0.5	NH_4NO_3	2.46	2.01	2.57	2.06			71BLb	
0.5	$NaClO_4$	2.618	β_3=	7.59*	2.44*			74LVa	
0.25		2.588	1.84*	β_4=	9.97*				
1.00		2.663	1.79*	β_4=	10.29*				
2.00		2.745	β_3=	8.25*	2.67*				
4.00		3.44*							
3.0		2.92	2.01	3.84	2.64			77FOa	
0.15		2.55	2.43	2.42	2.19			82NVa	37 °C
0.10	$NaNO_3$	2.51						82SSa	
0.15		2.98*	2.65*					83ERa	37 °C
Cd^{2+}									
0.15	KNO_3	β_2=	5.07*	1.39*	1.02*			54LC	
0.15		2.80	2.10	1.55	1.13			53TW	
0.1		2.71	2.00	1.35				71BLb	
0.5		3.11*	2.69*	2.30*	1.9*	1.6*		83LWa	
0.5	NH_4NO_3	2.68	2.02	1.35	1.02			70BLa	
0.5	$NaNO_3$	2.98	2.08	0.94	0.79			88EAb	
1.0		2.78	2.07	1.57	0.72	0.93*		86JAa	
1.0		2.69	1.62	1.17	1.59*			85KIa	
0.15		2.737						83ERa	37 °C
0.1		2.71						82SSa	
2.0		2.7	1.3*	1.3*	1.7*			81SJa	
0.5	$NaClO_4$	2.76	2.10	1.45	1.17			78MHa	

0.5		2.718	1.98					74LVa
0.25		2.699	2.03*					
1.00		2.768	1.989					
2.00		2.892	2.155	1.95				
4.00		3.09*						
1.0		2.70	2.40	1.60	0.95	0.6*	0.8*	68ISa
3.0		3.09	2.41	1.79	1.22			81GSa
1.0		2.70	2.40	1.53	0.97	0.58*	0.77*	75JEa
Hg^{2+}								
0.15	?	β_2=	16.74*					60BWa
0.058	KCl	3.57*	3.38*					61SM
0.5	$NaClO_4$	9.64	8.54					78MHa
3.0		9.18	9.01					77SJc
Pb^{2+}								
2.0	$NaNO_3$	2.9	1.4	2.0				85SSe
0.5		1.1	0.99					77HMb
Pd^{2+}								
?	KNO_3	6.40						88SKa
Ag^{+}				β_2				
1.0	KNO_3	3.11	3.73	6.84				60GG
1.0		3.05	3.83	6.88				64BWa
0.1		3.17	4.02	7.19				66DGb
0.058	KCl	3.78*	3.16*	6.94				61SM
0.5	KNO_3	3.31*	3.48*	6.79				85BGa
0.5		2.96	3.99	6.95				79BBa
0.5		2.70	4.18	6.88				70BLa
1.0		3.08	3.87	6.95				69NNa
0.5	NH_4NO_3	4.0*	2.88*	6.88				71BLb
3.0	$NaClO_4$	3.336	4.22	7.56				79GSb
Hf^{4+}								
0.1	KNO_3	7.02						76EWa

A critical evaluation of these mixed hydroxo- and chloro-complexes (as well as other mixed complexes with imidazole) will not be performed in the present evaluation due to the absence of comparable data.

As expected, Mn(II) forms weak complexes with imidazole. According to Table 6 there is an acceptable agreement in reported K-values except for those presented by 58ME. The reason for this divergence is not obvious by reading the corresponding paper. The high stability ($K_3 = K_2$) of the tris complex as reported by 89BLa must be regarded as doubtful.

Only two studies are reported with respect to Fe(II)- imidazole complexation. The work by 61SM is rejected because reported values of K_1 and K_2 are even greater that those for higher transition metals (e. g. Co(II), Zn(II)).

A series of CoL_n^{2+} complexes with n ranging from 1 to 6 has been reported. Usually K_n is greater than K_{n+1} except for values reported by 83LWa and 71BLb, who reported K_4 greater than K_3. This reflects the problems associated with the determination of stability constants at high ligand concentrations, rather than a coordination shift from octahedral to tetrahedral, which also has been discussed (83LWa). Reported values for K_5 and K_6 (log K 0–0.70) must also be regarded as doubtful as an accurate determination of these constants requires measurements at very high ligand concentrations, which introduces uncertainties as discussed above. The work by 74LVa was rejected because inappropriate speciation schemes were given. The values by 83ERa were also rejected due to too high K_1 and K_2 values. The most reliable values are given by 66SKf, 58MEa, 82SSa, 81FGa and 68ISa. Based upon these data sets recommended values were evaluated.

It can be noted that the different K_n -values show a small ionic strength dependence. This also seems to decrease with increasing n.

A situation similar to Co(II) is met with the Ni(II)- system. K_1 to K_6 values are reported. However, for the same reasons as given above, K_5 and K_6 values presented are regarded as doubtful. In 55LCa and 71BLb these constants were evaluated from $\bar{n}$ data less than four, which is inadequate. 83ERa and 74LVa were not evaluated because of inconsistent speciation models. Consistency in the remaining data set made it possible to present recommended values for K_1 to K_4.

The most frequently studied metal ion is Cu(II). As can be seen from Table 6 most of the values listed vary between 4.1–4.7(log K_1), 3.3–4.0 (log K_2), 2.8–3.3 (log K_3) and 2.0–2.7 (log K_4). This variation is small if one takes into account the quite broad range in ionic strengths (0.1–3.0) that has been studied. The general trend indicates upon a steady decrease in K_n with increasing n. Several values by 74LVa do not show this behaviour and were rejected. The study by 61JWa was performed in a sulphate medium (0.3M), with a possible formation of binary and/or ternary Cu(II)-sulphato complexes, which were not accounted for. For similar reasons a study in a KCl medium was excluded (Cu(II)-chloro complexation). The remaining data made it possible to give recommended values for K_1 to K_4.

Only two studies (72SJa and 83LWa) have been reported in which experimental average ligand numbers exceed the value of four. Though it seems likely that CuL_5 and CuL_6 should exist in aqueous solutions at high ligand concentrations, definitive answers to their stabilities must await further investigations.

The speciation of the Zn(II) - imidazole system is characterised by the formation of a series of ZnL_n^{2+} complexes with n ranging from 1 to 4. The stability sequence of the corresponding stepwise constants shows K_3 to be of the same magnitude or even greater than K_2. This behaviour has been attributed to a coordination shift from octahedral to tetrahedral as the tris - complex is formed. Data that were excluded from the recommended values are: 63CCb , 83ERa (both these sets deviate significantly from the bulk of published constants) and 74LVa, which contains incomplete speciation schemes.

Data for Cd(II) - imidazoles show good internal consistency except for some studies (54LCa,83LWa,85KIa,81SJa, 74LVa (parts)). For reasons discussed above the stability of possible pentakis- and hexakis- imidazole complexes must be regarded as doubtful.

Mercury(II) imidazoles have been the subject of four studies. Hg(II) typically binds two ligands very strongly in a linear configuration and shows only a small tendency to form tris and tetra coordinated species. This is also obvious from presented data in Table 6, showing upon the formation of HgL^{2+} and HgL_2^{2+}. The constants presented by 61SM are obviously wrong, most likely due to the presence of a strongly complexing agent (Cl^-) in the medium used. As the number of data are too limited to provide recommended constants, reported constants are regarded as tentative.

The Ag(I) ion also shows a preference for linear coordination, reflected in K_2 - values greater than K_1. This is also obvious from Table 6 except for results by 71BLb. The study by 61SM in a chloride medium is rejected. Furthermore, in 85BGa the difference in the two constants is too small to be in agreement with the others, hence these data are excluded as well. It is interesting to note that the agreement in reported β_2 - values is very good, whereas there is a significant scatter in K_1. This fact reflects the problems associated with a determination of a species (AgL^+) formed in small amounts.

There seems to be a fair agreement in reported β_2 - values of the Cu(I) - imidazole system, whereas only one K_1- value is given. Only tentative values have been assigned in the Cu(I) system.

For the remaining metal ions Pb(II), Pd(II) and Hf(IV) data are too scarce to allow a rigid evaluation.

Recommended and tentative values for the stability constants of imidazole complexes with metal ions are given in Table 7.

Metal Histamines Besides the earth alkaline metals Be(II), Mg(II) and Ca(II), the 3d metals as well as Ag(I), Cd(II) and Hg(II) have been studied with respect to histamine complexation (cf. Table 8). The most frequently reported speciation schemes are a series of ML_n -complexes with n=1,2,(3). In these complexes L acts as a bidentate ligand forming a six membered ring with the metal ion. Furthermore, protonated species, MHL and MHL_2 have been proposed in the alkaline earth's system (85RRc) and with Ni(II)

(78SKa), Cu(II) (87DZa, 80GMb, 80NSb), Zn(II) (70DOd, 78SKa) and Cd(II) (81AAc). In these complexes data clearly indicate the presence of a protonated imidazole nitrogen, hence the metal ion is monodentately coordinated to the amino group.

Table 7 Recommended and tentative logarithmic values of the stability constants of imidazole complexes with metal ions. The estimated errors in the recommended constants are ± 0.05 (log $K > 2$), ± 0.1 ($1 < \log K < 2$) and ± 0.2 ($0 < \log K < 1$). *C* is defined according to equation (3).

M^{z+}	K_n	$I = 0$	$I = 0.1$	$I = 0.5$	$I = 1.0$	$I = 3.0$	C	Cat.
Mn^{2+}	K_1	1.2	1.2	1.3			0.18	T
	K_2	0.8	0.8	0.9				T
Fe^{2+}	K_1	1.8	1.8					T
	K_2	1.2	1.2					T
Co^{2+}	K_1	2.46	2.47	2.50	2.54	2.70	0.08	R
	K_2	1.96	1.97	2.00	2.03	2.17	0.07	R
	K_3	1..50	1.50	1.52	1.53	1.59	0.03	R
	K_4	1.0	1.0	1.0	1.0	1.0	0.0	T
	K_5	?						
	K_6	?						
Ni^{2+}	K_1	3.02	3.03	3.08	3.13	3.35	0.11	R
	K_2	2.50	2.51	2.54	2.58	2.74	0.08	R
	K_3	2.00	2.01	2.04	2.07	2.21	0.07	R
	K_4	1.46	1.47	1.49	1.51	1.61	0.05	T
	K_5	?						
	K_6	?						
Cu^{2+}	K_1	4.18	4.20	4.26	4.34	4.66	0.16	R
	K_2	3.49	3.51	3.57	3.65	3.97	0.16	R
	K_3	2.94	2.95	3.00	3.06	3.30	0.12	R
	K_4	2.24	2.25	2.31	2.38	2.66	0.14	R
	K_5	0.6	0.6	0.6	0.7	1.0	0.14	T
	K_6	0.1	0.1	0.2	0.2	0.4	0.1	T
Zn^{2+}	K_1	2.55	2.56	2.61	2.67	2.91	0.12	R
	K_2	2.35	2.37	2.40	2.01	2.01		T
	K_3	2.22	2.23	2.27	2.57	3.84		T
	K_4	2.02	2.03	2.07	2.06	2.64		T
Cd^{2+}	K_1	2.66	2.67	2.73	2.79	3.05	0.13	R
	K_2	2.04	2.05	2.10	2.16	2.40	0.12	R
	K_3	1.43	1.44	1.49	1.55	1.79	0.12	R
	K_4	1.05	1.06	1.08	1.10	1.20	0.05	T
	K_5	?						
	K_6	?						
Hg^{2+}	K_1			9.64		9.18		T
	β_2			18.18		18.19		T
Cu^{+}	K_1		5.78					T
	β_2		11.0					T
Ag^{+}	K_1	2.92	2.93	2.99	3.06	3.34	0.14	R
	β_2	6.71	6.74	6.85	6.99	7.55	0.28	R

Table 8. Stability constants (logarithmic values) of metal complexes of histamine. Unless otherwise stated the constants are valid at 25 °C

I	Medium	K_1	K_2	K_3	β(MHL)	Ref.	Cat.
Be^{2+}							
0.12	KCl	7.12	5.35			70Caa	D
Mg^{2+}							
0.1	KNO$_3$				12.25	85RRc1)	D
Ca^{2+}							
0.1	KNO$_3$				12.13	85RRc1)	D
Mn^{2+}							
0.1	KNO$_3$				12.83	85RRc1)	Rj
0.2		2.98				71RMd2)	T
0.1	KCl	3.33				84DMc	T
Fe^{2+}							
1.0	KNO$_3$	9.60	6.49			56HF3)	Rj
0.058	KCl	5.80	4.26			61SM	Rj
Fe^{3+}							
0.058	KCl	3.72				61SM	Rj
Co^{2+}							
0.1	KNO$_3$	5.98				88RRc1)	D
0.15		4.89	3.54			69PSc4)	T
0.2		5.16	3.64			71RMd	T
0.5		5.30				83LWa	T
1.0		5.34	3.76			56HF3)	T
0.1	KCl	5.07	4.27			84DMc	D
0.135		5.27	3.68	2.03		55MA3)	T
0.1	?	5.03	3.74			69EHc	T
0.01	?	5.2				60HJ	D
0-corr		5.08	3.75	1.88		60NF3)	T
Ni^{2+}							
0.1	KNO$_3$	6.84	5.08	3.13		70DOd	R
0.1		6.36				85RRc1)	D
0.15		6.601	4.84	2.97		68PSf4)	T
0.2		6.70	5.03			71RMd	T
0.2		6.83				63CCb	T
0.5		6.87	5.03			83LWa	T
1.0		6.84	4.96	3.08		55MA3)	T
0.2	KCl	6.85	5.08	3.20	11.56	78SKa	R
0.135		6.88	5.03	3.09		55MA	R
0.3	NaClO$_4$	6.84	5.04	3.15		67HWa	R
0.1	?	6.76	5.02	3.11		69EHc	T
0.01	?	6.84	5.08	3.06		62HJa	R
0-corr.		6.77	5.01	3.25		60NF3)	T
Cu^{2+}							
0.1	KNO$_3$	9.57	6.57		12.88	87 DZa	R
					21.835)		T

0.1		(8.98)				85RRc1)	D
		9.27					
0.1		9.56	6.55		12.88	80GMb	R
					21.825)		T
0.1		9.56	6.57			70EH	R
0.1		9.48	6.42			64DCa	T
0.15		(9.28)	(6.30)			67PSc4)	T
		9.62	6.59				
0.16		9.56	6.37			70MBb	T
0.2		9.53	6.21			71RMd	T
0.2		9.59	6.52			79MBb	R
0.2		9.43				63CCb	D
0.5		9.42	6.57			83LWa	T
0.1	KCl	9.46	6.48			84DMc	T
0.135		9.55	6.48			55MA	R
0.2		9.58	6.48		21.795)	78SKa	R
0.2		9.60	6.49			73GSb	R
0.2	$NaClO_4$	(9.79)	(6.98)			84PBd3)	D
		9.94	7.10				
0.3		9.56	6.64			67HW	T
0.15		(9.24)	(6.92)		(13.46)	80NSb4)	D
		9.58	7.21		13.97		
1.5	K_2SO_4	9.83	6.77			66ZAa	Rj
1.5		9.45	6.51			66ZAa	Rj
0.1	?	9.56	6.57			69EHc	R
0.1	?	9.67	6.44			69HGb	T
0.01	?	9.55	6.49			62HJa	T
0-corr		(9.50)	(6.45)			60NF3)	T
		9.65	6.57				
Zn^{2+}							
0.1	KNO_3	(6.11)				85RRc1)	Rj
		6.25					
0.1		5.25	4.95		11.64	70DOb	R
0.2		5.27	4.96			79MBa	T
0.2		5.15	4.84			71RMd	T
0.2		5.62				63CCb	Rj
0.5		5.69				83LWa	D
0.058	KCl	5.38	4.46			61SM	D
0.1		5.17	4.56			84DMc	D
0.2		5.56	4.73		11.78	78SKa	D
Cd^{2+}							
0.1	KNO_3	4.76	3.15	2.02	11.53	81AAc	T
0.1			8.57(β_2)			64ARb	Rj
0-corr		4.80	3.39			60NF3)	T
Hg^{2+}							
0.058	KCl	6.01	4.62			61SM	Rj
Ag^{+}							
0.058	KCl	4.86				61SM	Rj

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1) 35 °C. 2) 15 °C. 3) 30 °C. 4) 37 °C. 5) $\beta(CuHL_2)$

In the Cu(II) - system deprotonation of the binary CuL_n^{2+} complexes is observed (64DCa, 66PSc, 66ZAa, 76DOb,78SKa, 80GMb, 84ACb) This has been interpreted as due to the formation of mixed hydroxo complexes *viz.* $CuL(OH)^+$, and $Cu_2(OH)_2L_2^{2+}$ and imidazole/imidazolate species in which the equatorial coordination sphere is N- saturated (e.g. $CuL(H_{-1}L)^+$ and $Cu(H_{-1}L)_2$, (78SKa)) .

The beryllium system has been studied by 70CAa. The reported K_1 and K_2 values are surprisingly high considering the fact that Be(II) preferably coordinates to oxygen donor groups. A closer inspection of the equilibrium analysis clearly revealed this to be inadequate. Therefore these constants are regarded as doubtful.

The complex formation reactions between histamine and Mg(II), Ca(II) or Mn(II) are, according to 85RRc, described by a single MHL^{3+} complex. It seems unlikely that such a complex should prevail in these systems without the formation of any binary M - L complex. Consequently, these results are regarded as doubtful as well.

The results given by 71RMd and 84DMc with respect to Mn(II) complexation are more likely.

Unexpectedly high stabilities are also reported for Fe(II) complexation (56HFa, 61SM). These values probably reflects the difficulties in handling the very oxygen sensitive Fe(II) systems and are rejected. The very strong hydrolytic properties of Fe(III) and its tendency to form colloidal suspensions make equilibrium studies in Fe(II) systems with ligands forming less stable complexes difficult. The value given by 61SM is thus regarded as doubtful.

An inspection of stability constants for Co(II) - histamine complexes shows upon a good agreement in the different *K*- values valid at 25 °C. (The constants at higher temperatures were not included in the evaluation as no reliable enthalpy values are available). The different log K_1 values vary between 5.03 (I = 0.1 M) and 5.30 (I = 0.5 M) and $3.54 \leq \log K_2 \leq 3.74$ (I = 0.1–0.2 M) except for the K_2 - value given by 84DMc, which is regarded as doubtful.

The Ni(II) - system was evaluated in a similar way i.e., data at higher temperatures were excluded. Remaining data show upon good internal consistency, which made it possible to calculate averaged values to get recommended or tentative values.

The most frequently studied metal ion with respect to histamine complexation is Cu(II). Studies have been performed in KNO_3, KCl, K_2SO_4 and $NaClO_4$ media of varying ionic strengths The constants show a very small ionic strength dependence and it is difficult to see any changes in the K_n - values due to medium composition. The constants determined in a 1.5 M sulphate medium were excluded from the evaluation due to possible formation of mixed sulphato complexes. Furthermore, divergent (85RRc, 84PBd, 80NSb), values were omitted before recommended or tentative values were identified.

In the Zn(II)-studies the ratio log K_1/K_2 equals 0.3 in NO_3^- media whereas this ratio is 0.6–0.9 in Cl^- media. This significant difference indicates that the chloride ions take part in the complexation thereby leading to erroneous conclusions about the speciation scheme in corresponding media. The low K_1/K_2 ratio in nitrate media probably explains the somewhat too high values of K_1 reported by 63CCa and 83LWa , who neglected the formation of ZnL_2^{2+} in their studies.

There is only one reliable study (81AAc) of Cd(II) - histamine complexation. The others are based on wrong speciation schemes (53PEa, 64ARb) or give incomplete information about the experimental procedures (60NF).

The studies (61SM) of the Hg(II) and Ag(I) systems are both rejected. Both metal ions form strong complexes with the medium anion (Cl^-) chosen and the constants presented are not evaluated by considering the likely formation of mixed chloro complexes.

Recommended and tentative values for the stability constants of histamine complexes with metal ions are listed in Table 9.

Table 9. Recommended and tentative values (25°C) for the stability constants of histamine complexes with metal ions.

M^{z+}	*I*	*log K₁*	*log K₂*	*logK₃*	Cat.
Mn^{2+}	0.1	3.3(2)			T
Co^{2+}	0.1	5.16(10)	3.65(7)	(2.0)	R (T)
Ni^{2+}	0.1–0.2	6.82(5)	5.05(3)	3.12(5)	R
Cu^{2+}	0.1	9.56(6)	6.50(10)	12.88 1)	R
				21.82 2)	T
Zn^{2+}	0.1	5.21(5)	4.92(5)		R
				11.72 1)	T
Cd^{2+}	0.1	4.78	3.27	2.0	T
				11.53 1)	T

1) log β(MHL). 2) log $\beta(MHL_2)$

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