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## CRITICAL EVALUATION OF STABILITY CONSTANTS OF PHOSPHONIC ACIDS\*\*

(IUPAC Technical Report)

Prepared for publication by

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# Critical evaluation of stability constants of phosphonic acids

## (IUPAC Technical Report)

*Abstract:* Available experimental data on stability constants of proton and metal complexes for 10 phosphonic acids [methylphosphonic acid, 1-hydroxyethane-1,1-diylbisphosphonic acid, dichloromethylenebisphosphonic acid, aminomethanephosphonic acid, *N*-(phosphonomethyl)glycine, imino-*N,N*-bis(methylenephosphonic acid), *N*-methylamino-*N,N*-bis(methylenephosphonic acid), nitrilotris(methylenephosphonic acid), 1,2-diaminoethane-*N,N,N',N'*-tetrakis(methylenephosphonic acid), and diethylenetriamine-*N,N,N',N'',N''*-pentakis(methylenephosphonic acid)], published in 1950–1997, have been critically evaluated. For the latter phosphonate, all the data are rejected, as well as protonation constants  $[HL]/[H][L]$  for three other ligands. Higher-quality data are selected and presented as “Recommended” and “Provisional”.

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### 1. INTRODUCTION

Organophosphonate chelating compounds are widely used in a broad variety of applications, particularly those compounds listed in Table 1. Their ability to prevent precipitation of calcium salts at substoichiometric concentrations (threshold effect) finds wide application in water treatment for scale inhibition [98N, 96GB, 88DT, 85K, 83M]. Phosphonates, particularly EDTPH and DTPPH, are used extensively in laundry detergents [92H]. These materials are also used as corrosion inhibitors, in industrial cleaning and in peroxy bleach stabilization [92H, 88DT, 85K]. Uses of organophosphonates span applications in flame-resistant polymers [88RD], photographic processing [88HK], ore flotation (aminophosphonic surfactants) [87CC], actinide separation processes [94N, 93LS, 93NR, 90HD], and analytical chemistry [87VW, 85AL]. Recently, organophosphonates have been identified as promising reagents for the creation of so-called “structurally tailored” materials [92BV, 92ZC, 91CM, 88CL] and

**Table 1** Ligands considered.

Semisystematic name <sup>a</sup>	Acronym	Number of references found	
		[98A]	[97C]
Methylphosphonic acid	MPA, H <sub>2</sub> mpa	14	5
1-Hydroxyethane-1,1-diylbisphosphonic acid	HEDPA, H <sub>4</sub> hedpa	57	29
Dichloromethylenediphosphonic acid	CMDPA, H <sub>4</sub> cmdpa	6	6
Aminomethanephosphonic acid	AMPH, H <sub>2</sub> amph	12	8
<i>N</i> -(Phosphonomethyl)glycine	PMG, H <sub>3</sub> pmg	11	8
Imino- <i>N,N</i> -bis(methylenephosphonic acid)	IDPH, H <sub>4</sub> idph	6	6
<i>N</i> -Methylamino- <i>N,N</i> -bis(methylenephosphonic acid)	MIDPH, H <sub>4</sub> midph	2	0
Nitrilotris(methylenephosphonic acid)	NTPH, H <sub>6</sub> ntph	26	15
1,2-Diaminoethane- <i>N,N,N',N'</i> -tetrakis(methylenephosphonic acid)	EDTPH, H <sub>8</sub> edtpH	23	14
1,4,7-Triazaheptane- <i>N,N,N',N'',N''</i> -pentakis(methylenephosphonic acid); Diethylenetriamine- <i>N,N,N',N'',N''</i> -penta(methylenephosphonic acid)	DTPPH, H <sub>10</sub> dtpph	9	5

<sup>a</sup>In this Report, semisystematic names that have been most frequently encountered in the literature are used. The corresponding IUPAC systematic names are the following: Methylphosphonic acid (MPA); (1-Hydroxyethane-1,1-diyl)bis(phosphonic acid) (HEDPA); (Dichloromethylene)bis(phosphonic acid) (CMDPA); (Aminomethyl)phosphonic acid (AMPH); [(phosphonomethyl)-amino]acetic acid or *N*-(phosphonomethyl)glycine (PMG); (iminodimethylene)bis(phosphonic acid) (IDPH); [(methylimino)-dimethylene]bis(phosphonic acid) (MIDPH); [Nitrilotris(methylene)]tris(phosphonic acid) (NTPH); [Ethylenebis(nitrilodimethylene)] tetrakis(phosphonic acid), EDTPH; [(phosphonomethyl)imino]bis(ethylenenitrilodimethylene) tetrakis(phosphonic acid) (DTPPH).

microporous materials [96YS], in catalysis [97KS], and in the electrochemical treatment of polluted soils [99PA, 96PY].

The high biological activity of carboxyalkylphosphonates, aminoalkylphosphonates, and alkylenediphosphonates makes them useful agents as components of microfertilizers and pesticides in agriculture, as well as drugs and diagnostic reagents in biology and medicine [97BK, 97KZ, 95B, 95K, 94SC, 93CB, 93M, 91DJ, 89HO, 89JB, 88CF, 86M, 83JS, 90SW, 88SH, 89ZI, 93SC]. Annual industrial output of organophosphonates is in the thousands of tons [98N, 92H].

The broad and intensive applications of organophosphonates require reliable data on the stability constants of the corresponding complexes in order to permit equilibrium modeling and prediction of the important technological, environmental, and pharmacokinetic equilibria. As phosphonates resist biodegradation, chemical speciation calculations based on numerical equilibrium data are of extreme importance for applications such as environmental science, waste management, agriculture, scale inhibition, magnetic resonance imaging, behavior of radiopharmaceuticals in blood plasma, and many others [98DB, 98N, 97BK, 95JW, 89MB].

The data of interest are partly accumulated in some monographs [95K, 90KA, 88DT, 79B], reviews [97N, 90K, 92H, 89B, 83R, 75KD, 57FD] and compilations of stability constants [89MS, 71SM]. Recently, two computer databases have become commercially available [98A, 97C]. The IUPAC Stability Constants Database, SC-Database, [98A, 95IU] is the more comprehensive, Table 1. For organophosphonates, some data in the "critically evaluated compilations" [89MS, 93NI] are not consistent with later, more precise results. These are therefore rejected in the present work.

This study attempts to evaluate all reported proton and metal ion binding constants for the most commonly used organophosphonates and to recommend a reasonable set of values for use in chemical speciation calculations. Published material embraces in total more than 100 organophosphonate reagents of both aliphatic and aromatic origin. Most of them are represented by a single publication or by just a few papers of poorer quality and thus could not be critically evaluated following the accepted

IUPAC rules [77B, 75CS]. Among the complexants with poor numerical data there are ligands of considerable practical interest such as phosphonoacetic acid (7 references found) and 1,2,4-tricarboxybutane-2-phosphonic acid, PBTC (one reference [99SE]). On the whole, the number of organophosphonates that permit the comparison of data presented by independent groups of scientists appears to be surprisingly small. Within these, a priority was given to alkylphosphonates and aminoalkylphosphonates of high industrial (HEDPA, PMG, NTPH, EDTPH, DTPPH) or medical (HEDPA, CMDPA, EDTPH) importance and to some ligands with more simple structures (MPA, AMPH, IDPH, MIDPH) that represent complex forming fragments and decomposition products of the former ones, for example, AMPH which is the main metabolic product of the highly effective broad-spectrum herbicide glyphosate (PMG) [92SC].

This review is generally based on the data published in the period 1965–1996, but some earlier and later publications are also included. The data collection embraced databases [98A, 97C], *Chemical Abstracts*, and the personal collections of the authors. The names of journals are presented in original transcription with pages of the English version (if any) given in parentheses.

## 2. GENERAL PHYSICO-CHEMICAL PROPERTIES OF ORGANOPHOSPHONATES

Phosphonates generally have their greatest affinity for metal ions when present as fully dissociated species (highly alkaline solutions). They are especially effective in complexing strongly hydrolyzed cations, such as Al(III), Tl(III), Au(III), Zr(IV), Th(IV), Pt(II), etc. It is reported that NTPH in 10-fold excess can hold Au(III) in aqueous solution even at pH 11, while EDTA can stabilize Au(III) as a complex only at pH <9 [85GS]. Titanium(IV) complexes with HEDPA at 1:1 ratio do not decompose at pH 12 [78CM]. <sup>31</sup>P NMR reveals that 0.1M Tl(III) solutions in the presence of 0.2 M NTPH can resist hydrolytic decomposition at pH >12 [91P], and with glycine-*N,N*-bis(methylenephosphonic acid) up to pH 10 [98PA]. Complexes of HEDPA with Nb(V) [83KC, 77GC], B(III) [97KK, 89SS, 86KC], U(VI) [93N], Re [97DZ], and <sup>99m</sup>Tc [87GD] seem to be more stable than those of its carboxy-analog malonate and even than of EDTA, while the glyphosate complex with Fe(III) is more stable than that of IDA [89MB]. Unfortunately, most of these systems are not yet characterized in terms of numerical equilibrium constants. Thus, the quantitative data published to date and considered in the present review probably do not reflect the most important features of complex formation by the organophosphonates.

Protonation of organophosphonate metal–ligand complexes (ML) does not necessarily lead to their decomposition. This can be illustrated by an X-ray structure of Er(H<sub>3</sub>hedpa)H<sub>2</sub>hedpa·5H<sub>2</sub>O [89SZ], which clearly indicates that even highly protonated HEDPA anion is capable of forming chelate compounds. Normally, the free ligands and the organophosphonate complexes ML, which exist above pH 8, are highly soluble in water. However, for MH<sub>x</sub>L<sub>y</sub> complexes this is generally valid only for sufficiently basic solutions and/or for those systems where there is a substantial excess of ligand over metal. In all other cases, polymerization can take place, a process which strongly affects the quality of stability constant measurements. An association of mononuclear particles results generally in formation of visible inhomogeneity due to precipitation. However, rather frequently these processes are not visible. For example, absolutely transparent solutions of 1:1 Al(III)–NTPH at 5 <pH <6 can have <sup>31</sup>P NMR line broadening due to polymerization so large that the spectra cannot be detected even at 0.2 M concentrations [84LP]. In contrast, the <sup>1</sup>H, <sup>31</sup>P, <sup>23</sup>Na, and <sup>35</sup>Cl NMR-studies of 0.02 M La-NTPH solutions clearly indicate formation of colloids at pH 6–9 even at metal/ligand ratios of 1:1 and 1:2 [94LP, 94LA]. This effect is not surprising, bearing in mind that most ligands with the phosphonate group can act as scale inhibitors. In water treatment technology, the concentrations of organophosphonates used as scale inhibitors are within the range of 0.0001–0.000 01 M. Slight heterogeneity cannot be excluded at 0.001 M reagent concentrations as normally used for potentiometry. In so far as all the ligands of interest inhibit scale formation of calcium carbonates or sulfates, they could also act in the same manner as self-stabilizers of fine colloidal particles of their own insoluble compounds.

The effect stated above arises from the ability of the phosphonate group to act not only as a monodentate but also as a bidentate and even terdentate center. This is clearly demonstrated by X-ray studies of HEDPA-complexes [92TK, 90TP, 72U] and is also supported by light-scattering experiments [71W]. Generally, increasing pH, ligand denticity, and ligand/metal ratio and decreasing coordination number of the cation leads to a decrease of heterogeneous effects and vice versa. The problem of solid-phase formation is more critical for HEDPA and NTPH than for EDTPH. Reference [74TK] reports the solubility of YHhedpa·5H<sub>2</sub>O to be about 0.000 022 M at 22 °C. Unfortunately, this property of the organophosphonates is still not sufficiently well recognized by many groups that measure the stability of these complexes. Any stability constant measurements for organophosphonates should be preceded by preliminary NMR and light-scattering experiments.

Besides issues of heterogeneity, ion association (polymerization) in homogeneous solutions of organophosphonates should also be taken into account. This can be illustrated by the complex [Al<sub>2</sub>H<sub>2</sub>(ntph)<sub>2</sub>]<sup>4+</sup> [91P, 84LP]. The dimer, unambiguously detected by NMR at 0.2–0.1 M concentration level, is characterized by protonated uncoordinated nitrogen atoms and three structurally unequivalent phosphonate groups, one of which is easily identified as bidentate by paramagnetic NMR-contrasting [91P, 91PL]. Thus, three rather unusual 8-membered chelate rings are formed along with one 12-membered ring. This leads to a very stable structure. At pH 6–9, the robust dimer coexists in equilibrium with the monomer. Below pH 6, further polymerization takes place, and at pH <5 a precipitate forms. Formation of large, stable 8-membered chelate rings seems to be rather common for NTPH and its derivatives [96SI, 94LP, 94LA, 91P, 89SA]. Sometimes, polymerization can be the cause of an unusual sequence of complex formation steps. For 1:2 beryllium:HEDPA systems BeL<sub>2</sub> complexes are sequentially transformed into MH<sub>x</sub>L + “free” H<sub>p</sub>L, then into the *bis*-complex Be(H<sub>y</sub>L)<sub>2</sub> and then back into BeH<sub>z</sub>L + “free” H<sub>q</sub>L ( $x < y < z$ ) as the pH changes from 12 to 1.5 [87GL].

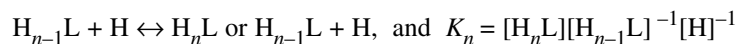
Many association processes, including the formation of colloids, have very slow kinetics. This causes the pH to drift with time. Sometimes, periods of hours up to several weeks are needed to reach equilibrium after ligand and metal solutions are mixed [91P, 90VS, 87GL, 77MR, 71W, 67H]. Precautions are also needed to ensure adequate time delay in titrations between successive increments of titrant [67KL, 67H, 80M, 83FB, 83VZ, 88VS, 89KM, 96SI].

Phosphonates demonstrate a very high affinity for alkali metal ions. This observation is supported by a number of X-ray data for HEDPA complexes [79BS, 89SP, 89SZ]. For example, sodium exhibits the ability to form chelate rings including the coordination of the aliphatic hydroxy-group even with the triply protonated ligand NaH<sub>3</sub>hedpa·H<sub>2</sub>O [90SM]. The assignment of stability constants for the corresponding compounds NaHhedpa, NaH<sub>2</sub>hedpa, and even for NaH<sub>3</sub>hedpa [87MK, 72WF, 67CI] therefore seems to be reasonable.

Most organophosphonates are synthesized from phosphorous acid (made from PCl<sub>3</sub> and H<sub>2</sub>O) by reaction with formaldehyde and either ammonia (NTPH) or alkylamines (EDTPH, DTPPH). HEDPA is formed from PCl<sub>3</sub> and acetic acid or acetic anhydride. Impurities, consisting of H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>3</sub>, and ligands of lower denticity, are quite common for phosphonates [66MI, 84RK, 93IL]. Unlike aminocarboxylates, these ligands form crystals only with some difficulty and are usually distributed commercially as 25 to 60% aqueous solutions of acids or sodium salts with technical grade purity. Until recently, only a few reagents were commercially available as reagent grade products. Among these are HEDPA and EDTPH. For the latter ligand, Martell has questioned the purity of samples used before 1976 [76MM]. Thus, the problem of purity is especially important for this group of reagents.

### 3. PRESENTATION OF EQUILIBRIUM DATA AND ABBREVIATIONS USED

The protonation constants of ligands are presented as  $K_n$  where equilibrium is represented as



In all cases, L indicates the totally deprotonated species. HEDPA is treated as  $H_4L$ . To indicate HEDPA molecules with five protons released ( $hedpa^{5-}$ ), a symbol  $H_{-1}L$  is used. The symbol “ $I$ ” indicates ionic strength, and “ $\rightarrow$ ” implies an extrapolation to  $I = 0$ . Equilibria for metal-complexes are self-explanatory:  $M + L \leftrightarrow ML$  is presented as  $M + L$  or  $K_{ML}$ ;  $M + H + L \leftrightarrow MHL$  is presented as  $M + H + L$ ;  $M + HL \leftrightarrow MHL$  is presented as  $M + HL$  and so on. Unless specified otherwise, the numerical data in the text refer to  $I = 0.1$  M and 25 °C.

In potentiometric titrations with a glass electrode, the calibration technique governs the type of constant calculated. Concentration constants determined by calibrating the electrode system with solutions of known hydrogen ion concentration (e.g., a monoprotic strong acid) or by the conversion of pH values using the appropriate hydrogen ion activity coefficient are indicated in the text as “Conc.”. Mixed constants [91SM, 84P] obtained when standard buffer solutions of known hydrogen activity are used (e.g., potassium hydrogenphthalate buffer with pH 4.008 at 25 °C) include both activity (hydrogen ions) and concentration (all other participants of the complexation equilibrium) terms and are marked as “Mix”. Following the reasons described elsewhere [91KS, 91SM, 84P], priority is given to concentration constants.

The methods used in papers selected for evaluation are denoted by the following symbols:

gl	glass electrode (pH-metry)
EMF	metal electrode (emf measurement)
red	redox electrode (emf measurement)
ix	ion-exchange
sp	spectrophotometry
NMR	nuclear magnetic resonance
elph	electrophoresis
cal	calorimetry
ext	extraction

The ligands other than organophosphonates are denoted as follows:

Gly	glycine, Hgly
IDA	iminodiethanoic acid, $H_2ida$
MIDA	<i>N</i> -methyliminodiethanoic acid, $H_2mida$
NTA	nitrilotriethanoic acid, $H_3nta$
EDTA	1,2-diaminoethane- <i>N,N,N',N'</i> -tetraethanoic acid, $H_4edta$
bipy	bipyridyl

#### 4. DATA EVALUATION CRITERIA

Data published on organophosphonates have been evaluated by applying the following general criteria [97LP, 96YO, 91KS, 91SM]:

- clear definition of constants reported (i.e., unambiguous specification of complex stoichiometry, MHL,  $M(OH)L$ , etc., of complex stability constants and whether concentration or mixed constants were calculated)
- the extent to which essential reaction conditions (the purity of the ligand, temperature, ionic strength, the nature of the supporting electrolyte, account of metal–ligand reaction kinetics, ligand:metal ratio, etc.) have been specified
- the soundness of calibration of the apparatus used (e.g., calibration of the electrode system for potentiometric measurements)
- the maintenance of constant temperature and ionic strength during titrations
- reliable treatment of the experimental data (e.g., careful consideration of all possible species formed: parent and mixed hydroxo-complexes of readily hydrolysable metal ions, formation of

dimers and polymers, etc.)

- correct selection of auxiliary data from the literature (e.g., selection of the concentration constants of the proton complexes for the evaluation of magnetic relaxation or polarographic measurements carried out on metal–ligand systems only).
- details of the calculation method used

On the basis of these criteria, experimental data have been examined and roughly grouped into two categories: “accepted” and “rejected”. Among those data that passed the preliminary acceptance criteria, those that exhibited the best agreement were selected for further treatment. These were averaged and rounded and, depending on the standard deviations (SD), the rounded average values were regarded as **Recommended (R)**:  $SD < 0.05$  for H-complexes (e.g., H + L or H + ML) and  $< 0.1$  for metal-complexes (M + L or M + HL) or **Provisional (P)**:  $0.05 < SD < 0.2$  for H-complexes and  $0.1 < SD < 0.2$  for metal-complexes. The SD indicates, therefore, an agreement among the selected data and is given in tables in parentheses after each constant.

In a few specified cases when evaluation identified some mistake in the determination of the constants, which are nevertheless of semiquantitative value, the criteria  $0.2 < SD < 0.3$  ( $\lg K_{HL}$ ) and  $0.2 < SD < 1.0$  ( $\lg K_{ML}$ ) were used to indicate values that the present authors assess as being reliable. Such data are not included in tables, but are given in comments. The same treatment has been used for some papers that do not have evident errors but reveal gaps in the description of some important experimental details.

Some papers with data that are rejected contain important supplementary information (normally spectroscopic) that could be helpful in future research. Thus, all the references with rejected (or partly rejected) data are listed at the beginning of any section devoted to the particular ligand, and the cations studied are indicated. The rejected data are, however, not listed in the tables. The references that are cited but not included in tables could also be:

- earlier publications from one group;
- communications with possibly correct data but inadequate description of experimental conditions;
- communications that reviewers could not access in the original version (in this case, an original reference is normally followed by *Chem. Abstr.* citation);
- publications of the same research group with stability constant data that completely duplicate the cited one;
- publications that need further independent evaluation (this situation includes the cases where two independent research groups offer data that formally meet the above-stated requirements, but due to some hidden systematic errors reveal very large numerical discrepancies); and
- publications that provide data for conditions that contrast with those for other data (e.g., high temperatures, water/ethanol solutions, ternary complexes, etc).

The ligands are considered in the order of increasing complexity. The stability constants of metal complexes are surveyed in the following groups: hydrogen ion, IA, IIA, IIIA, IVA, VA groups, 3d-group, 4d–5d, IIIB, and a group of 4f–5f metal ions. Complete information on the experimental conditions used in papers selected for evaluation is given before each table. The averaged stability constants (with standard deviation in parentheses) and their evaluation category are tabulated, together with the most important experimental information (medium, temperature) and the references assumed. Medium is indicated by a cation used (K, Na,  $\text{Me}_4\text{N}$ ) with a charge omitted for brevity. When the average value is derived from data obtained in different media, then symbols like Na/K are used.

The reviewers tried to avoid recalculations to a uniform ionic strength. The data listed therefore represent the average value of those from the original publications. Enthalpy values are omitted owing to the relatively low number of data published by independent groups.

The  $\text{H}_n\text{L}$  and ML stability constants published for MIDPH, IDPH, HEDPA, NTPH, EDTPH, and DTPPH are rather controversial. Several problems characterize the determination of stability constants

of organophosphonate ligands. These include (a) the low purity of NTPH, EDTPH, and DTPPH samples used; (b) the low solubility of some complexes formed by HEDPA, NTPH, EDTPH; (c) the formation of complexes with  $K^+$  and  $Na^+$  ions (commonly involved in the background electrolyte) by *all organophosphonates* studied; (d) the low purity of the  $(CH_3)_4NCl/(CH_3)_4NOH$  background electrolyte used as an alternative to Na/K salts/bases; and (e) the high uncertainty in the determination of very high first protonation constants for IDPH, MIDPH, NTPH, EDTPH, and DTPPH ( $12 < \lg K < 14$ ).

For example, competitive background sodium ion complexation is especially critical for  $\lg K(H + L)$  and  $\lg K(HL + H)$  values of HEDPA, as was clearly demonstrated in [83FB]:

Background salt	$\lg K(H + L)$	$\lg K(HL + H)$	$\lg K(H_2L + H)$
0.1 M $Me_4NCl$	11.19	7.03	2.78
0.1 M $NaCl$	10.20	6.78	2.76

Data of [87MK] for HEDPA indicate the same trend for KCl media:

Background salt	$\lg K(H + L)$	$\lg K(HL + H)$	$\lg K(H_2L + H)$
0.1 M $Bu_4NCl$	10.66	7.06	2.99
0.1 M $KCl$	10.15	6.68	2.62
0.1 M $NaCl$	10.05	6.65	2.51

Therefore, only the data in  $R_4NCl$  as supporting electrolyte have been taken for critical evaluation of HEDPA and CMDPA protonation constants. The same influence of K/Na salts was observed for MIDPH, NTPH, and EDTPH [90B]. For the MPA analog—hydroxymethylphosphonic acid ( $HOCH_2PO_3H_2$ )—it was found that  $\lg K_{KL} = 0.34$ ;  $\lg K_{NaL} = 0.61$  [72WF]. In this respect, the  $\lg K_{ML}$ —data listed in Tables 2, 5, 6, and 8 are therefore likely to represent “apparent” or “conditional constants” according to A. Ringbom [63R] except where precise experiments with  $R_4NX$  background salts are done. The concept presented in [63R] gives the term “conditional constant” a somewhat broader significance than a simple account of hydrolytic reactions of the complexing agent and of the metal, but includes the whole series of side reactions. In this respect, an ignorance of phosphonate complexation by a background alkali cation gives not a “concentration constant”, but a “conditional constant” as far as this constant is *not* constant, but depends on the experimental *conditions*: the nature and the concentration of background cation. For  $M + HL$  equilibria, the influence of  $K^+$  or  $Na^+$  for monoaminophosphonates is expected to be negligible.

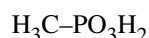
In case of IDPH, MIDPH, NTPH, EDTPH, and DTPH, most research groups used the glass electrode for estimation of the first protonation constants ( $12 < pK < 14$ ), which led to significant errors both in  $\lg K_1$  and  $\lg K_{ML}$ . An error in  $\lg K(M + L)$  is limited by the error in  $\lg K(H + L)$ . Both constants have, therefore, one and the same systematic error associated with only one wrong figure:  $\lg K_1$ . In order to eliminate it, the values  $\lg K(M + HL)$  in Tables 7, 9, and 10 have been recalculated in the following way:  $\lg K(M + HL) = \lg K(M + L) + \lg K(ML + H) - \lg K(H + L)$ . In this case, a systematic error introduced by  $\lg K(M + L)$  is compensated by the  $\lg K(H + L)$ , which have the same numerical value, but opposite sign. Thus, for IDPH, NTPH, and EDTPH, the reviewers report only the data for  $\lg K(M + H_iL; i > 0)$ .

These problems, coupled with the rather small number of publications for some metal–ligand combinations, have limited the number of “Recommended” values proposed.

Critically evaluated data are presented in Tables 2–10.



## 5. METHYLPHOSPHONIC ACID, MPA



Cations studied:

<b>H<sup>+</sup></b> : 99AV, 96AK, 96SM, 93CB, 93CG, 92SC, 86NI, 84AH, 79WN, 77KT, 75KW 72EZ, 68DM, 67BE, 57FD, 54BE, 53CK 49C, 47RC, 30N	<b>Ba<sup>2+</sup></b> : 92SC <b>Al<sup>3+</sup></b> : 96AK <b>VO<sup>2+</sup></b> : 96SM <b>Mn<sup>2+</sup></b> : 92SC <b>Fe<sup>2+</sup></b> : 86NI <b>Co<sup>2+</sup></b> : 92SC <b>Ni<sup>2+</sup></b> : 92SC <b>Cu<sup>2+</sup></b> : 93CB, 93CG, 92SC, 86NI, 79WN <b>Zn<sup>2+</sup></b> : 92SC	<b>Cd<sup>2+</sup></b> : 92SC <b>Y<sup>3+</sup></b> : 69DZ <b>Ln<sup>3+</sup></b> : 69DZ <b>Nd<sup>3+</sup></b> : 89AC <b>Am<sup>3+</sup></b> : 72EZ, 67BE <b>Cm<sup>3+</sup></b> : 72EZ, 67BE <b>Pm<sup>3+</sup></b> : 72EZ, 67BE
<b>Na<sup>+</sup></b> : 99AV <b>Be<sup>2+</sup></b> : 99AV, 68DM <b>Mg<sup>2+</sup></b> : 92SC, 86NI, 75KW <b>Ca<sup>2+</sup></b> : 92SC, 86NI, 79WN <b>Sr<sup>2+</sup></b> : 92SC		

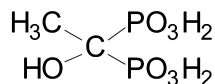
Experimental conditions:

- $I = 0.1 \text{ M NaNO}_3$ , 25 °C, gl, Mix.: 93CB, 92SC  
 $I = 0.1 \text{ M KNO}_3$ , 25 °C, gl, Conc.: 79WN  
 $I = 0.2 \text{ M KCl}$ , 25 °C, gl, Conc.: 96SM, 96AK  
 $I = 0.2 \text{ and } 0.5 \text{ M NH}_4\text{ClO}_4$ , 25 °C, gl, ix, Mix.: 67BE  
 $I = 0.5 \text{ M (CH}_3)_4\text{NCl}$ , 25 °C, gl, Conc.: 99AV

**Table 2** Recommended and provisional data for MPA, 25 °C.

Cation	Equilibrium	$I/M$	$\lg K$	Category	References
H <sup>+</sup>	H + L	0.1 (Na/K)	7.54 (0.02)	P	92SC, 79WN
		0.2 (K)	7.42 (0.02)	P	96SM
		0.5 [(CH <sub>3</sub> ) <sub>4</sub> N]	7.54 (0.02)	P	99AV
	HL + H	0.1 (K)	2.19 (0.02)	P	79WN
		0.2 (K/NH <sub>4</sub> )	2.13 (0.04)	R	96SM, 67BE
Na <sup>+</sup>	M + L	0.5 [(CH <sub>3</sub> ) <sub>4</sub> N]	0.5 (0.1)	P	99AV
		0.5 [(CH <sub>3</sub> ) <sub>4</sub> N]	6.2 (0.1)	P	99AV
Be <sup>2+</sup>	M + L	0.1 (Na)	1.9 (0.1)	P	92SC
Mg <sup>2+</sup>	M + L	0.1 (Na/K)	1.6 (0.1)	R	92SC, 79WN
Ca <sup>2+</sup>	M + L	0.1 (Na)	1.4 (0.1)	P	92SC
Sr <sup>2+</sup>	M + L	0.1 (Na)	1.3 (0.1)	P	92SC
Ba <sup>2+</sup>	M + L	0.2 (K)	6.50 (0.05)	P	96AK
		0.2 (K)	12.3 (0.1)	P	96AK
		0.2 (K)	5.87 (0.04)	P	96SM
VO <sup>2+</sup>	M + HL	0.2 (K)	2.13 (0.04)	P	96SM
	M + L	0.1 (Na)	2.5 (0.1)	P	92SC
Mn <sup>2+</sup>	M + L	0.1 (Na)	2.2 (0.1)	P	92SC
Co <sup>2+</sup>	M + L	0.1 (Na)	2.3 (0.1)	P	92SC
Ni <sup>2+</sup>	M + L	0.1 (Na/K)	3.50 (0.05)	R	93CB, 79WN
Cu <sup>2+</sup>	M + L	0.1 (Na)	2.6 (0.1)	P	92SC
Zn <sup>2+</sup>	M + L	0.1 (Na)	2.9 (0.1)	P	92SC
Cd <sup>2+</sup>	M + HL	0.5 (NH <sub>4</sub> )	1.8 (0.2)	P	67BE
Am <sup>3+</sup>	M + HL	0.5 (NH <sub>4</sub> )	1.9 (0.2)	P	67BE
Cm <sup>3+</sup>	M + HL	0.5 (NH <sub>4</sub> )	1.7 (0.2)	P	67BE
Pm <sup>3+</sup>	M + HL	0.5 (NH <sub>4</sub> )			

## 6. 1-HYDROXYETHANE-1,1-DIYLBISPHOSPHONIC ACID, HEDPA



*Common names:* Etidronic acid, IONQUEST 201 (Albright & Wilson, aqueous solution of HEDPA), DEQUEST 2040 (Monsanto, aqueous solution of HEDPA); Na(K)<sub>2</sub>H<sub>2</sub>L, Calcimax, Didronel, Diphos, Etidron, Ksidiphon.

HEDPA has been known since 1898 [898BH]. Solid HEDPA is one of the few reagents of interest that is commercially available from Merck, Proctor & Gamble, Albright & Wilson, IREA (Russia), and other chemical companies at reagent grade purity.

*Cations studied*<sup>a–g</sup>:

<b>H<sup>+</sup></b> : 98AP, 98DK, 97DB, 97ZJ, 96SM, 95DS, 95NC <sup>g</sup> , 95NR <sup>g</sup> , 93K, 93N, 90NH, 89KA, 89KK, 89MN, 89VZ, 87AS, 87MK, 87PA, 85LF, 84CL, 84VO, 83FB, 83VK, 83VZ, 83YM, 80KW, 80M, 80ZR, 77CP, 76DG, 72KB, 72KZ, 72WF, 71WF, 68CI, 67CI, 67GQ, 67KL	<b>Sr<sup>2+</sup></b> : 80RZ, 67KL <b>Ba<sup>2+</sup></b> : 80RZ <b>Al<sup>3+</sup></b> : 67KL <b>Ga<sup>3+</sup></b> : 89KK, 80MM <sup>e</sup> , 71CA <b>Ge(IV)</b> : 83SB <b>Sn<sup>2+</sup></b> : 84CL <b>Pb<sup>2+</sup></b> : 89NO <b>VO<sup>2+</sup></b> : 98DK, 96SM <b>Cr<sup>3+</sup></b> : 99DP <b>Mn<sup>2+</sup></b> : 89NO, 80ZR, 67KL <b>Mn<sup>3+</sup></b> : 78P <b>Fe<sup>2+</sup></b> : 97BD, 67KL <b>Fe<sup>3+</sup></b> : 90VK, 87PA, 73KG, 72KD, 67KL <b>Co<sup>2+</sup></b> : 80ZR, 67KL <b>Ni<sup>2+</sup></b> : 97BD, 95DS, 89VK, 89KM, 87SA, 84AS, 80RA, 80ZR, 76RL, 67KL <b>Cu<sup>+</sup></b> : 99AP <b>Cu<sup>2+</sup></b> : 97DB, 95DS, 89KM, 89VA <sup>g</sup> , 89NO, 87AS, 87VS, 85GA, 80ZR, 80KW, 73VN, 71CA, 71WF, 67KL <b>Zn<sup>2+</sup></b> : 97BD, 97ZJ, 95DS, 95VK, 87VA, 80ZR, 76DG, 67KL	<b>Ag<sup>+</sup></b> : 80ZR <b>Cd<sup>2+</sup></b> : 97BD, 95DS, 89N, 80ZR, 78MZ <b>ZrO<sup>2+</sup></b> : 67KL <b>MoO<sup>2+</sup></b> : 90TK <b>Pd<sup>2+</sup></b> : 80ZR <b>Y<sup>3+</sup></b> : 87AM <b>La<sup>3+</sup></b> : 87AM <b>Sm<sup>3+</sup></b> : 97ZJ, 87AM <b>Nd<sup>3+</sup></b> : 87AM <sup>f</sup> , 87AP <b>Eu<sup>3+</sup></b> : 95NC <sup>g</sup> , 95NR <sup>g</sup> , 90NH, 87AM, 72LM <b>Gd<sup>3+</sup></b> : 87AM <b>Tb<sup>3+</sup></b> : 87AM <b>Dy<sup>3+</sup></b> : 87AM <b>Th<sup>4+</sup></b> : 91N, 67KL <b>UO<sup>2+</sup></b> : 93N <b>Am<sup>3+</sup></b> : 72LM
<b>Li<sup>+</sup></b> : 72WF, 67CI <b>Na<sup>+</sup></b> : 87MK, 87VS, 86VK, 85VK, 83FB, 83VZ, 72WF, 67CI <b>K<sup>+</sup></b> : 87MK, 72WF, 67CI <b>Cs<sup>+</sup></b> : 67CI <b>Be<sup>2+</sup></b> : 67KL <sup>d</sup> <b>Mg<sup>2+</sup></b> : 97ZJ, 93K, 89MN, 86VA, 86VK, 86VZ, 84VA, 83YM, 80ZR, 76DG, 72WF, 68CI <b>Ca<sup>2+</sup></b> : 97ZJ, 97DB, 93K, 89MN, 86VA, 86VK, 86VZ, 85LF, 84CL, 84VA, 83FB, 83YM, 80KW, 80ZR, 76DG, 72WF, 71GC, 71W, 68CI, 67KL		

*Experimental conditions:*

*I* = 1.0 M (CH<sub>3</sub>)<sub>4</sub>NCl, 25 °C, gl, Conc.: 93K

*I* = 0.5 M (CH<sub>3</sub>)<sub>4</sub>NCl, 25 °C, gl, Conc.: 68CI, 67CI

*I* = 0.1 M (CH<sub>3</sub>)<sub>4</sub>NCl, 25 °C, gl, Conc.: 72WF, 71WF; Mix.: 84CL, 83FB, 67GQ

*I* = 0.2 M KCl, 25 °C, gl, Conc.: 96SM

*I* = 0.1 M KCl, 25 °C, gl, Conc.: 98DK, 97DB, 67KL; calibration unknown: 76DG

*I* = 2.0 M Na/HClO<sub>4</sub>, 25 °C, ext, Conc.: 90NH; *I* = 0.1 M Na/HClO<sub>4</sub>, ext, Conc.: 93N

**Table 3** Recommended and provisional data for HEDPA<sup>a</sup>, 25 °C.

Cation	Equilibrium	I/M	lgK	Category	References	
H <sup>+</sup> <sup>a,b</sup>	H + L	0.1 (Me <sub>4</sub> N)	11.2 (0.2)	P	84CL, 83FB, 67GQ	
		0.5 (Me <sub>4</sub> N)	11.41 (0.05)	P	68CI	
		1.0 (Me <sub>4</sub> N)	11.14 (0.05)	P	93K	
	HL + H	0.1 (Me <sub>4</sub> N)	7.02 (0.02)	R	84CL, 83FB, 72WF, 67GQ	
		0.5 (Me <sub>4</sub> N)	6.97 (0.05)	P	68CI	
		1.0 (Me <sub>4</sub> N)	6.93 (0.05)	P	93K	
	H <sub>2</sub> L + H	0.1 (Me <sub>4</sub> N)	2.7 (0.2)	P	98DK, 84CL, 83FB, 72WF, 67GQ	
		0.5 (Me <sub>4</sub> N)	2.54 (0.05)	P	68CI	
		1.0 (Me <sub>4</sub> N)	2.53 (0.05)	P	93K	
	H <sub>3</sub> L + H	1.0 (Me <sub>4</sub> N)	1.43 (0.05)	P	93K	
Li <sup>+</sup>		M + L	0.5 (Me <sub>4</sub> N)	3.4 (0.1)	P	67CI
		M + HL	0.1 (Me <sub>4</sub> N)	1.4 (0.1)	P	72WF
Na <sup>+</sup>	M + L	0.5 (Me <sub>4</sub> N)	1.1 (0.1)	P	67CI	
		0.1 (Me <sub>4</sub> N)	0.8 (0.1)	P	72WF	
	M + HL	0.5 (Me <sub>4</sub> N)	0.5 (0.1)	P	67CI	
K <sup>+</sup>	M + L	0.5 (Me <sub>4</sub> N)	1.8 (0.1)	P	67CI	
		0.1 (Me <sub>4</sub> N)	0.6 (0.1)	P	72WF	
	M + HL	0.5 (Me <sub>4</sub> N)	0.4 (0.1)	P	67CI	
Cs <sup>+</sup>	M + L	0.5 (Me <sub>4</sub> N)	1.6 (0.1)	P	67CI	
	M + HL	0.5 (Me <sub>4</sub> N)	0.2 (0.1)	P	67CI	
Mg <sup>2+</sup>	M + L	0.1 (Me <sub>4</sub> N)	7.3 (0.2)	P	72WF	
		0.5 (Me <sub>4</sub> N)	6.4 (0.1)	P	68CI	
		1.0 (Me <sub>4</sub> N)	7.2 (0.1)	P	93K	
	M + HL	0.1 (Me <sub>4</sub> N)	3.8 (0.1)	P	72WF	
		0.5 (Me <sub>4</sub> N)	3.3 (0.1)	P	68CI	
		1.0 (Me <sub>4</sub> N)	3.1 (0.1)	P	93K	
	M + ML	0.1 (Me <sub>4</sub> N)	3.4 (0.2)	P	72WF	
		1.0 (Me <sub>4</sub> N)	2.9 (0.1)	P	93K	
	Ca <sup>2+</sup>	M + L	0.1 (Me <sub>4</sub> N)	6.4 (0.2)	P	84CL, 72WF
			0.5 (Me <sub>4</sub> N)	5.7 (0.1)	P	68CI
M + HL		0.1 (Me <sub>4</sub> N/K)	3.3 (0.2)	P	84CL, 72WF	
Sn <sup>2+</sup>	M + L	0.5 (Me <sub>4</sub> N)	3.6 (0.2)	P	68CI	
		0.1 (Me <sub>4</sub> N)	4.6 (0.1)	P	84CL, 97DB	
	M + HL	0.1 (Me <sub>4</sub> N)	15.7 (0.2)	P	84CL	
VO <sup>2+</sup>	M + HL	0.2 (K)	8.6 (0.2)	P	96SM	
Cu <sup>2+</sup>	M + L	0.1 (Me <sub>4</sub> N)	11.8 (0.2)	P	71WF	
	M + HL	0.1 (Me <sub>4</sub> N)	7.5 (0.1)	P	71WF	
	M + H <sub>2</sub> L	0.1 (Me <sub>4</sub> N)	4.3 (0.1)	P	71WF	
Zn <sup>2+</sup>	M + HL	0.1 (K)	5.1 (0.2)	P	97DB, 76DG	
Eu <sup>3+</sup>	M + H <sub>2</sub> L	2.0 (Na/H)	4.6 (0.2)	P	90NH	
	M + H + H <sub>2</sub> L	2.0 (Na/H)	6.4 (0.2)	P	90NH	
UO <sub>2</sub> <sup>2+</sup>	M + H + H <sub>2</sub> L	0.1 (Na/H)	8.0 (0.2)	P	93N	
	M + H <sub>3</sub> L	0.1 (Na/H)	5.5 (0.2)	P	93N	
	M + 2H <sub>2</sub> L	0.1 (Na/H)	11.8 (0.2)	P	93N	

<sup>a</sup>The first communication on this compound claimed isolation of the penta-basic salt of HEDPA [98BH]. However, attempts to repeat this result have all failed [77CP]. Numerous spectroscopic and physicochemical data on HEDPA solutions revealed no evidence of HOC-group dissociation up to pH 13 [92TK, 91P, 90BM, 90TP, 87GL, 83VK, 72KZ].

The X-ray structures for HEDPA complexes CuH<sub>2</sub>L(bipy)·3H<sub>2</sub>O [89SM], K<sub>4</sub>Na<sub>2</sub>CuL·6H<sub>2</sub>O [85PJ], CaH<sub>2</sub>L·H<sub>2</sub>O [72U], Er(H<sub>3</sub>L)H<sub>2</sub>L·5H<sub>2</sub>O [89SM], (NH<sub>4</sub>)<sub>3</sub>MoO<sub>2</sub>H<sub>3</sub>L<sub>2</sub>·6.75H<sub>2</sub>O [90TP], and Na<sub>4</sub>NH<sub>4</sub>MoO<sub>2</sub>(HL)L·5H<sub>2</sub>O [90KT], as well as ESR data on aqueous solutions of V(IV)-HEDPA complexes [96SM], indicate that in most cases either the hydroxy group is not coordi-

nated at all or that it coordinates without dissociation. Therefore, the formation of  $MH_{-1}L$  species can probably be neglected in stability constant evaluations for normal and protonated complexes of alkaline earths, 3d-cations ( $M^{2+}$ ) and f-cations ( $M^{3+}$ ). Thus, HEDPA was treated as  $H_4L$ .

In contrast, it was established by X-ray analysis that HEDPA is penta-basic for W(VI) and Mo(VI) in  $[C(NH_2)_3]_5[WO_3(H_{-1}L)] \cdot 4.5H_2O$  [94ST] and  $K_8Mo_6O_{17}(H_{-1}L)_2 \cdot 10H_2O$  [92TK]. This was confirmed by  $^{31}P$  NMR analysis of these complexes in an aqueous phase [92TK], and by ESR for V(IV) in aqueous solutions of  $[VOH_{-1}L]$  at pH 12–14 [96SM]. This raises the problem of knowing a reasonable  $\lg K$  value for  $H_{-1}L + H \leftrightarrow L$ . The corresponding NMR-measurements indicate:  $\lg K(H_{-1}L + H) > 14.5$ , 24 °C,  $I = 3.4$  M  $Me_4NCl$  [99PN].

<sup>b</sup>Experimental data published on the first protonation constant  $K(H + hedpa^{4-})$  reveal a very high disagreement for 0.1 M  $R_4NCl$  medium [87MK, 85LF, 84CL, 83FB, 72WF, 67GQ]. At the same time, most of these values are not consistent with generally more accurate measurements done at higher  $R_4NCl$  ionic strengths [93K, 68CI], see Fig. 1. The observed disagreement among protonation constants measured in  $R_4NCl$  media could partly arise from the low purity of both  $R_4NOH$  and  $R_4NCl$ . Our analysis of some commercial samples of 4M  $R_4NOH$  solution indicated 4.9 mg/l Ca; 22 mg/l Na; and 75 mg/l Mg. All these cations would influence the protonation constants calculated for HEDPA. It is noted that the base  $R_4NOH$  prepared by ion exchange cannot be recommended for accurate work [72DM]. Those references that do not specify purification of background and bases (dark triangles, Fig. 1) demonstrate lower values even relative to  $KNO_3$  medium (circles).

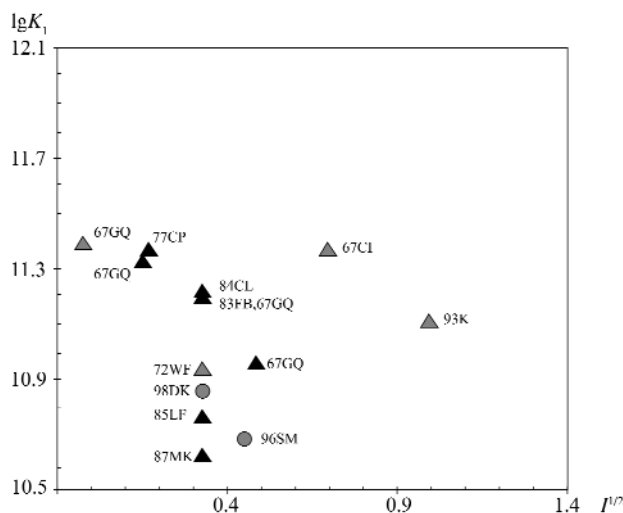
<sup>c</sup>The ML stability constants of all cations are treated as reliable if measured in  $R_4NCl$  media. For MHL complexes, competition by potassium does not seem to be significant, and the corresponding data measured in  $KNO_3$  (as well as that for  $MH_2L$  in NaCl solutions) are also included.

<sup>d</sup>The stability constant  $\lg K(Be + HL) = 7(1)$  (0.1 M  $KNO_3$ , 25 °C, gl, Conc. [67KL]) reflects the really high affinity of HEDPA toward Be(II) in comparison with alkaline earths or with classical complexants like NTA, EDTA.

<sup>e</sup>The potentiometric curve for the Gallium(III) complex is complicated by turbidity at pH >4 because of precipitation of  $Ga(OH)_3$ . However,  $\lg K(Ga + HL) = 10.5$  (0.5) evaluated at pH <4 ( $I = 0.1$  M  $KNO_3$ , 25 °C, gl, Conc. [80MM]) indicates that the affinity of HEDPA for Ga(III) is the highest among all known bidentate ligands.

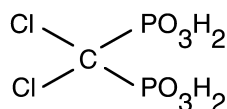
<sup>f</sup>Measurements of stability constants of rare earths are hindered by precipitation. Further, protonation of  $LnHL$  leads to formation of the soluble complex  $LnH_2L$  and then to total decomposition of the complex at pH <−0.4 [87AP]. Due to the excellent resolution of the  $Nd^{3+}$  and  $[NdH_2L]^+$  visible absorption bands, the value  $\lg K(Nd + H_2L) = 5.6$  (0.2) can be treated as reliable ( $I \sim 0.7$  M  $HClO_4$ , 25 °C, sp, Conc. [87AP]).

<sup>g</sup>Only thermochemical data.



**Fig. 1** Dependence of  $\lg K_1$  for HEDPA on ionic strength in  $Me_4NCl$  medium. Triangles indicate  $Me_4NCl$  and circles -  $KCl/KNO_3$  medium. Dark symbols indicate papers that give no special indication of tetramethylammonium salt purification.

## 7. DICHLOROMETHYLENEBISPHOSPHONIC ACID, CMDPA



Common name: Clodronic acid.

Cations studied<sup>a,b</sup>:

**H<sup>+</sup>**: 93K, 93KL, 84CL, 83FB, 76DG, 67GQ      **Sn<sup>2+</sup>**: 84CL  
**Ca<sup>2+</sup>**<sup>a</sup>: 93K, 93KL, 84CL, 83FB, 76DG  
**Na<sup>+</sup>**: 93K, 83FB  
**Mg<sup>2+</sup>**: 93K, 93KL, 76DG      **Zn<sup>2+</sup>**<sup>b</sup>: 76DG

Experimental conditions:

*I* = 1.0 and 0.1 M (CH<sub>3</sub>)<sub>4</sub>NCl, 25 °C, gl, Conc.: 93K, 93KL

*I* = 0.1 M (CH<sub>3</sub>)<sub>4</sub>NCl, 25 °C, gl, Mix.: 84CL, 83FB, 67GQ

**Table 4** Recommended and provisional constants for CMDPA at 25 °C and *I* = 0.1 M Me<sub>4</sub>NCl.

Cation	Equilibrium	lg <i>K</i>	Category	References
H <sup>+</sup>	L + H	9.5 (0.1)	P	93K, 93KL, 84CL, 83FB, 67GQ
	HL + H	5.94 (0.03)	R	93K, 93KL, 84CL, 83FB
	H <sub>2</sub> L + H	2.0 (0.2)	P	93K, 83FB, 67GQ
Na <sup>+</sup>	M + L	1.4 (0.2)	P	93K, 83FB
	M + HL	0.3 (0.1)	P	93K
	M + ML	0.8 (0.1)	P	93K
Mg <sup>2+</sup>	M + L	6.2 (0.1)	P	93KL
	M + HL	3.2 (0.1)	P	93KL
	M + ML	3.0 (0.1)	P	93KL
Ca <sup>2+</sup>	M + L	5.9 (0.2)	R	93KL, 84CL
	M + HL	3.15 (0.05)	P	93KL, 84CL
Sn <sup>2+</sup>	M + L	13.6 (0.1)	P	84CL
	M + HL	8.9 (0.1)	P	84CL
	M + ML	8.0 (0.1)	P	84CL

<sup>a</sup>lg*K*(Ca + CaL) = 3.3 (0.3), 0.1 M (CH<sub>3</sub>)<sub>4</sub>NCl, 25 °C, gl, Conc. [93KL, 84CL].

<sup>b</sup>lg*K*(Zn + HL) = 4.6 (0.3), 0.1 M KCl, 25 °C, gl, calibration unknown [76DG].

## 8. AMINOMETHANEPHOSPHONIC ACID, AMPH



Cations studied:

**H<sup>+</sup>**<sup>a</sup>: 97BL, 94SC, 79WB, 78WA, 78WN, 76SK, 72AU, 71GD, 71WN, 71WT      **Mn<sup>2+</sup>**: 94SC      **Zn<sup>2+</sup>**: 94SC, 79WB, 76SK, 71WT  
**Co<sup>2+</sup>**: 94SC, 79WB, 76SK, 72UA, 71WT      **Cd<sup>2+</sup>**: 94SC

**Mg<sup>2+</sup>**: 94SC, 79WB, 71WT  
**Ca<sup>2+</sup>**: 94SC, 79WB, 71GD,  
 71WN, 71WT  
**Sr<sup>2+</sup>**: 94SC  
**Ba<sup>2+</sup>**: 94SC

**Ni<sup>2+</sup>**: 94SC, 79WB, 76SK,  
 72UA, 71GD, 71WT  
**Cu<sup>2+</sup>**: 94SC, 79WB, 76SK,  
 74WN, 72UA, 71GD, 71WT

**Pd<sup>2+</sup>**: 97BL<sup>b</sup>  
**Pt<sup>2+</sup>**: 97BL<sup>b</sup>

*Experimental conditions:*

*I* = 0.1 M NaNO<sub>3</sub>, 25 °C, gl, Mix.: 94SC

*I* = 0.1 M KNO<sub>3</sub>, 25 °C, gl, Conc.: 97BL, 79WB

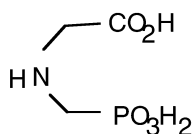
**Table 5** Recommended and provisional data for AMPH, 25 °C.

Cation	Equilibrium	<i>I/M</i>	lg <i>K</i>	Category	References
H <sup>+</sup> <sup>a</sup>	L + H	0.1 (K)	10.04 (0.02)	R	97BL, 79WB
	HL + H	0.1 (Na/K)	5.41 (0.02)	R	97BL, 94SC, 79WB
Mg <sup>2+</sup>	M + L	0.1 (Na/K)	2.00 (0.05)	R	94SC, 79WB
	M + HL	0.1 (Na/K)	1.3 (0.1)	R	94SC, 79WB
Ca <sup>2+</sup>	M + L	0.1 (Na/K)	1.67 (0.05)	R	94SC, 79WB
	M + HL	0.1 (Na/K)	1.06 (0.05)	R	94SC, 79WB
Sr <sup>2+</sup>	M + L	0.1 (Na)	1.34 (0.05)	P	94SC
	M + HL	0.1 (Na)	0.79 (0.07)	P	94SC
Ba <sup>2+</sup>	M + L	0.1 (Na)	1.17 (0.05)	P	94SC
	M + HL	0.1 (Na)	0.67 (0.06)	P	94SC
Mn <sup>2+</sup>	M + L	0.1 (Na)	3.6 (0.1)	P	94SC
	M + HL	0.1 (Na)	1.8 (0.1)	P	94SC
Co <sup>2+</sup>	M + L	0.1 (Na/K)	4.5 (0.1)	R	94SC, 79WB
	M + HL	0.1 (Na/K)	1.6 (0.1)	R	94SC, 79WB
	M + 2L	0.1(K)	8.1 (0.2)	P	79WB
Ni <sup>2+</sup>	M + L	0.1 (Na/K)	5.30 (0.04)	R	94SC, 79WB
	M + HL	0.1 (Na/K)	1.6 (0.1)	R	94SC, 79WB
	M + 2L	0.1(K)	9.0 (0.1)	P	79WB
Cu <sup>2+</sup>	M + L	0.1 (Na/K)	8.10 (0.05)	R	94SC, 79WB
	M + HL	0.1 (Na/K)	2.6 (0.1)	R	94SC, 79WB
	M + 2L	0.1 (K)	14.7 (0.1)	P	79WB
Zn <sup>2+</sup>	M + L	0.1 (Na/K)	5.0 (0.1)	R	94SC, 79WB
	M + HL	0.1 (Na/K)	1.70 (0.06)	R	94SC, 79WB
Cd <sup>2+</sup>	M + L	0.1 (Na)	5.1 (0.1)	P	94SC
	M + HL	0.1 (Na)	2.0 (0.1)	P	94SC

<sup>a</sup>lg*K*(H<sub>2</sub>L + H) = 0.4 (0.2), *I* = 0.1 M KNO<sub>3</sub>, 25 °C, gl, Conc. [78WN].

<sup>b</sup>The values lg*K*(Pd + 2L) = 27.5 (0.5) and lg*K*(Pt + 2L) = 22(2) [97BL] (*I* = 0.1 M KNO<sub>3</sub>, 25 °C, gl, Conc.) could be accepted as being reliable.

**9. *N*-(PHOSPHONOMETHYL)GLYCINE, PMG**



*Common name:* Glyphosate

*Cations studied:*

<b>H<sup>+</sup></b> : 97BK, 90DL, 89SH, 88SR, 88VA, 86AH, 85MM, 84BM, 84VZ, 78MC, 76W, 75SM	<b>Al<sup>3+</sup></b> : 85MM <b>Mn<sup>2+</sup></b> : 85MM, 78MC <b>Fe<sup>2+</sup></b> : 85MM <b>Fe<sup>3+</sup></b> : 85MM <b>Co<sup>2+</sup></b> : 85MM <b>Ni<sup>2+</sup></b> : 93DL, 85MM	<b>Cu<sup>2+</sup></b> : 97BK, 94JK, 85MM, 78MC <b>Zn<sup>2+</sup></b> : 85MM, 78MC <b>Cd<sup>2+</sup></b> : 85MM <b>La<sup>3+</sup></b> : 85MM
<b>Mg<sup>2+</sup></b> : 85MM, 78MC		
<b>Ca<sup>2+</sup></b> : 88SR, 85MM, 78MC		

*Experimental conditions:*

*I* = 0.2 M KCl, 25 °C, gl, Conc.: 97BK

*I* = 0.1 M KNO<sub>3</sub>, 25 °C, gl: Mix. 78MC; Conc.: 88SR, 85MM

*I* = 0.1 M NaCl, 25 °C, gl, Mix.: 93DL

**Table 6** Recommended and provisional data for PMG, 25 °C.

Cation	Equilibrium	<i>I/M</i>	lg <i>K</i>	Category	References
H <sup>+</sup>	L + H	0.1 (K)	10.14 (0.02)	P	85MM
		0.2 (K)	10.03 (0.02)	P	97BK
	HL + H	0.1 (K)	5.46 (0.02)	P	85MM
		0.2 (K)	5.37 (0.02)	P	97BK
	H <sub>2</sub> L + H	0.1 (K)	2.22 (0.02)	P	85MM
0.2 (K)		2.13 (0.02)	P	97BK	
Mg <sup>2+</sup>	M + L	0.1 (K)	3.3 (0.1)	R	85MM, 78MC
	M + H + L	0.1 (K)	12.1 (0.1)	P	85MM
Ca <sup>2+</sup>	M + L	0.1 (K)	3.30 (0.05)	R	85MM, 78MC, 88SR
	M + H + L	0.1 (K)	11.5 (0.1)	P	85MM, 88SR
Al <sup>3+</sup>	M + L	0.1 (K)	13.7 (0.1)	P	85MM
	M + H + L	0.1 (K)	16.2 (0.1)	P	85MM
	M + 2L	0.1 (K)	22.1 (0.2)	P	85MM
Mn <sup>2+</sup>	M + L	0.1 (K)	5.50 (0.03)	R	85MM, 78MC
	M + H + L	0.1 (K)	12.3 (0.1)	P	85MM
	M + 2L	0.1 (K)	7.8 (0.1)	P	85MM
Fe <sup>2+</sup>	M + L	0.1 (K)	6.9 (0.1)	P	85MM
	M + H + L	0.1 (K)	12.8 (0.1)	P	85MM
	M + 2L	0.1 (K)	11.2 (0.1)	P	85MM
Fe <sup>3+</sup>	M + L	0.1 (K)	16.1 (0.1)	P	85MM
	M + H + L	0.1 (K)	17.6 (0.1)	P	85MM
	M + 2L	0.1 (K)	23 (0.2)	P	85MM
Co <sup>2+</sup>	M + L	0.1 (K)	7.2 (0.1)	P	85MM
	M + H + L	0.1 (K)	12.6 (0.1)	P	85MM
	M + 2L	0.1 (K)	11.1 (0.1)	P	85MM
Ni <sup>2+</sup>	M + L	0.1 (Na/K)	8.0 (0.1)	R	85MM, 93DL
	M + H + L	0.1 (Na/K)	13.3 (0.1)	R	85MM, 93DL
	M + 2L	0.1 (Na/K)	12.3 (0.1)	R	85MM, 93DL
Cu <sup>2+</sup>	M + L	0.1 (K)	11.90 (0.05)	R	85MM, 78MC
		0.2 (K)	11.7 (0.1)	P	97BK
	M + H + L	0.1 (K)	15.9 (0.1)	R	85MM, 78MC
		0.2 (K)	15.5 (0.1)	P	97BK

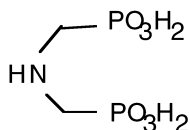
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**Table 6** (Continued)

Cation	Equilibrium	<i>I/M</i>	lg <i>K</i>	Category	References
Zn <sup>2+</sup>	M + 2L	0.1 (K)	16.0 (0.1)	P	85MM
		0.2 (K)	16.4 (0.1)	P	97BK
	M + L	0.1 (K)	8.7 (0.2)	P	85MM
Cd <sup>2+</sup>	M + 2L	0.1 (K)	11.7 (0.2)	P	85MM
	M + L	0.1 (K)	7.3 (0.1)	P	85MM
	M + H + L	0.1 (K)	12.6 (0.1)	P	85MM
La <sup>3+</sup>	M + 2L	0.1 (K)	10.9 (0.1)	P	85MM
	M + L	0.1 (K)	6.7 (0.1)	P	85MM
	M + H + L	0.1 (K)	13.6 (0.1)	P	85MM
	M + 2L	0.1 (K)	10.1 (0.1)	P	85MM

<sup>a</sup>lg*K*(H<sub>2</sub>L + H) = 0.5 (0.2), *I* ~ 1 M H/KNO<sub>3</sub>, 21 °C, NMR [89SH].

## 10. IMINO-*N,N*-BIS(METHYLENEDIPHOSPHONIC ACID), IDPH



Cations studied<sup>a,b</sup>:

<b>H<sup>+</sup></b> <sup>a</sup> : 97BK, 87VK <sup>b</sup> , 86AH, 85MM, 83VK, 83VT, 82BG, 79ZT	<b>Pb<sup>2+</sup></b> : 85MM <b>Mn<sup>2+</sup></b> : 85MM, 82BG <b>Fe<sup>2+</sup></b> : 85MM <b>Fe<sup>3+</sup></b> : 85MM	<b>Cu<sup>2+</sup></b> : 97BK, 85MM, 82BG, 79ZT <b>Zn<sup>2+</sup></b> : 85MM <b>Cd<sup>2+</sup></b> : 85MM <b>La<sup>3+</sup></b> : 85MM
<b>Mg<sup>2+</sup></b> : 85MM <b>Ca<sup>2+</sup></b> : 85MM, 82BG <b>Al<sup>3+</sup></b> : 85MM	<b>Co<sup>2+</sup></b> : 85MM, 82BG, 79ZT <b>Ni<sup>2+</sup></b> : 85MM, 82BG, 79ZT	

Experimental conditions:

*I* = 0.2 M KCl, 25 °C, gl, Conc.: 97BK

*I* = 0.1 M KNO<sub>3</sub>, 25 °C, gl, Conc.: 85MM

**Table 7** Provisional stability constants for IDPH, 25 °C, in KCl/KNO<sub>3</sub>.

Cation	Equilibrium	<i>I</i>	lg <i>K</i>	Category	References
H <sup>+</sup> <sup>a</sup>	HL + H	0.1	6.10 (0.02)	P	85MM
		0.2	6.10 (0.02)	P	97BK
	H <sub>2</sub> L + H	0.1	5.04 (0.02)	P	85MM
		0.2	4.85 (0.02)	P	97BK
Mg <sup>2+</sup>	M + HL	0.1	2.7 (0.1)	P	85MM
	ML + H	0.1	9.2 (0.1)	P	85MM
	MHL + H	0.1	5.2 (0.1)	P	85MM
Ca <sup>2+</sup>	M + HL	0.1	2.4 (0.1)	P	85MM
	ML + H	0.1	9.4 (0.1)	P	85MM

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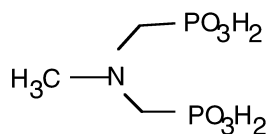


Table 7 (Continued)

Cation	Equilibrium	<i>I</i>	lg <i>K</i>	Category	References
Mn <sup>2+</sup>	MHL + H	0.1	5.4 (0.1)	P	85MM
	M + HL	0.1	3.6 (0.1)	P	85MM
	ML + H	0.1	8.1 (0.1)	P	85MM
Fe <sup>2+</sup>	MHL + H	0.1	4.9 (0.1)	P	85MM
	M + HL	0.1	3.6 (0.1)	P	85MM
	ML + H	0.1	6.7 (0.1)	P	85MM
Co <sup>2+</sup>	MHL + H	0.1	5.0 (0.1)	P	85MM
	M + HL	0.1	3.3 (0.1)	P	85MM
	ML + H	0.1	6.3 (0.1)	P	85MM
Ni <sup>2+</sup>	MHL + H	0.1	4.8 (0.1)	P	85MM
	M + HL	0.1	3.5 (0.1)	P	85MM
	ML + H	0.1	5.9 (0.1)	P	85MM
Cu <sup>2+</sup>	MHL + H	0.1	4.8 (0.1)	P	85MM
	M + HL	0.1	6.7 (0.1)	P	85MM
		0.2	6.78 (0.05)	P	97BK
	ML + H	0.1	4.6 (0.1)	P	85MM
		0.2	4.85 (0.05)	P	97BK
		0.2	3.75 (0.05)	P	97BK
Zn <sup>2+</sup>	MHL + H	0.2	3.75 (0.05)	P	97BK
	M + HL	0.1	4.7 (0.1)	P	85MM
	ML + H	0.1	6.5 (0.1)	P	85MM
Cd <sup>2+</sup>	MHL + H	0.1	5.4 (0.1)	P	85MM
	M + HL	0.1	4.5 (0.1)	P	85MM
	ML + H	0.1	6.0 (0.1)	P	85MM
Pb <sup>2+</sup>	MHL + H	0.1	3.2 (0.1)	P	85MM
	M + HL	0.1	6.2 (0.1)	P	85MM
	ML + H	0.1	6.8 (0.1)	P	85MM
La <sup>3+</sup>	MHL + H	0.1	4.4 (0.1)	P	85MM
	M + HL	0.1	7.6 (0.1)	P	85MM
	ML + H	0.1	9.2 (0.1)	P	85MM

<sup>a</sup>Potentiometric lg*K*<sub>1</sub>-data presented by [85MM, 97BK]: 10.97(0.03) [97BK] and 10.79 [85MM] disagree with NMR measurements: lg*K*<sub>1</sub> > 11(28 °C) [86AH] and differ greatly from those for MIDPH. <sup>b</sup>[87VK]: thermochemical data only.

## 11. *N*-METHYLAMINO-*N,N*-BIS(METHYLENEDIPHOSPHONIC ACID), MIDPH



Cations studied:

H<sup>+</sup><sup>a</sup>: 98KK, 93SK, 90B, 88LD,  
86AH  
Mg<sup>2+</sup>: 93SK, 88LD  
Ca<sup>2+</sup>: 93SK, 88LD  
Sr<sup>2+</sup>: 93SK, 88LD

Ba<sup>2+</sup>: 93SK, 88LD  
Mn<sup>2+</sup>: 93SK  
Fe<sup>2+</sup>: 93SK  
Co<sup>2+</sup>: 93SK, 88LD  
Ni<sup>2+</sup>: 93SK, 88LD

Cu<sup>2+</sup>: 98KK, 93SK, 88LD  
Zn<sup>2+</sup>: 93SK, 88LD  
Cd<sup>2+</sup>: 93SK, 88LD

*Experimental conditions:* $I = 0.1 \text{ M KNO}_3$ , 25 °C, gl, Conc.: 93SK $I = 0.1 \text{ M NaClO}_4$ , 25 °C, gl, Conc.: 88LD**Table 8** Recommended and provisional stability constants for MIDPH, 25 °C.

Cation	Equilibrium	$I(\text{M})$	$\lg K$	Category	References
$\text{H}^{+\text{a}}$	L + H	0.1(K)	12.1 (0.1)	P	93SK
	HL + H	0.1 (Na/K)	6.1 (0.1)	P	93SK, 88LD
	$\text{H}_2\text{L} + \text{H}$	0.1 (Na/K)	4.95 (0.05)	R	93SK, 88LD
	$\text{H}_3\text{L} + \text{H}$	0.1 (K)	1.3 (0.1)	P	93SK
$\text{Mg}^{2+}$	M + L	0.1 (Na/K)	5.1 (0.2)	P	93SK, 88DL
	M + HL	0.1 (K)	2.8 (0.2)	P	93SK
	ML + H	0.1 (K)	9.70 (0.05)	P	93SK
	MHL + H	0.1 (K)	5.0 (0.1)	P	93SK
$\text{Ca}^{2+}$	M + L	0.1 (Na/K)	4.6 (0.2)	P	93SK, 88DL
	M + HL	0.1 (K)	2.6 (0.2)	P	93SK
	ML + H	0.1 (K)	10.10 (0.04)	P	93SK
	MHL + H	0.1 (K)	5.1 (0.1)	P	93SK
$\text{Sr}^{2+}$	M + L	0.1 (K)	3.7 (0.2)	P	93SK
	M + HL	0.1 (K)	2.2 (0.2)	P	93SK
	ML + H	0.1 (K)	10.60 (0.04)	P	93SK
	MHL + H	0.1(K)	5.3 (0.1)	P	93SK
$\text{Ba}^{2+}$	M + L	0.1(K)	3.6 (0.2)	P	93SK
	M + HL	0.1(K)	2.1 (0.2)	P	93SK
	ML + H	0.1(K)	10.60 (0.04)	P	93SK
	MHL + H	0.1(K)	5.4 (0.1)	P	93SK
$\text{Mn}^{2+}$	M + L	0.1 (K)	8.2 (0.2)	P	93SK
	M + HL	0.1 (K)	4.1 (0.2)	P	93SK
	ML + H	0.1 (K)	7.90 (0.04)	P	93SK
	MHL + H	0.1 (K)	4.5 (0.1)	P	93SK
$\text{Fe}^{2+}$	M + L	0.1 (K)	9.1 (0.2)	P	93SK
	M + HL	0.1 (K)	4.0 (0.2)	P	93SK
	ML + H	0.1 (K)	7.00 (0.04)	P	93SK
	MHL + H	0.1 (K)	4.3 (0.1)	P	93SK
$\text{Co}^{2+}$	M + L	0.1 (Na/K)	9.3 (0.2)	P	93SK, 88LD
	M + HL	0.1 (Na/K)	3.9 (0.2)	P	93SK, 88LD
	ML + H	0.1 (Na/K)	6.53 (0.05)	R	93SK, 88LD
	MHL + H	0.1 (K)	4.4 (0.1)	P	93SK
$\text{Ni}^{2+}$	MHL + HL	0.1 (Na)	2.8 (0.1)	P	88LD
	M + L	0.1 (K)	9.6 (0.2)	P	93SK
	M + HL	0.1 (Na/K)	3.8 (0.2)	P	93SK, 88LD
	ML + H	0.1 (Na/K)	6.25 (0.04)	R	93SK, 88LD
$\text{Cu}^{2+}$	MHL + H	0.1 (K)	4.4 (0.1)	P	93SK
	MHL + HL	0.1 (Na)	3.0 (0.1)	P	88LD
	M + L	0.1 (Na/K)	14.3 (0.2)	P	93SK, 88LD
	M + HL	0.1 (K)	6.7 (0.2)	P	93SK
	ML + H	0.1 (Na/K)	4.6 (0.2)	P	93SK, 88LD
	MHL + H	0.1 (K)	3.4 (0.1)	P	93SK
	MHL + HL	0.1 (Na)	4.1 (0.2)	P	88LD

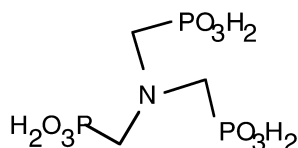
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**Table 8** (Continued)

Cation	Equilibrium	$I(M)$	$\lg K$	Category	References
$Zn^{2+}$	M + L	0.1 (K)	10.4 (0.2)	P	93SK
	M + HL	0.1 (K)	4.2 (0.2)	P	93SK
	ML + H	0.1 (K)	5.7 (0.2)	P	93SK
	MHL + HL	0.1 (Na)	4.1 (0.2)	P	88LD
$Cd^{2+}$	M + L	0.1 (K)	10.2 (0.2)	P	93SK
	M + HL	0.1 (K)	4.8 (0.1)	P	93SK
	ML + H	0.1 (K)	6.7 (0.1)	P	93SK
	MHL + H	0.1 (K)	4.4 (0.1)	P	93SK

<sup>a</sup>Like other polyphosphonic acids, MIDPH is expected to form complexes with  $K^+$  and  $Na^+$  [90B, 67CC]. On this basis, the values in Table 8 should be treated as conditional constants. In the absence of  $K^+$  and  $Na^+$  the protonation constant [ $\lg K(L + H)$ ] is estimated to be higher than 13 [67CC] and hence it is not accurately measurable from potentiometric titration. This estimation is in good agreement with  $^{31}P$  NMR measurements performed at 0 °C [96SI], which indicate that  $\lg K(L + H) \sim 12.5-13.0$ .

## 12. NITRILOTRIS(METHYLENephosphonic acid), NTPH



*Common names:* DEQUEST 2050 (Monsanto, aqueous solution), NTPH (IREA, solid white powder).

NTPH normally has impurities of phosphinic acid, phosphoric acid and sometimes MIDPH [84RK]. Its purification is comparatively easy, however some NMR assessment of sample purity is recommended.

*Cations studied* <sup>a-f</sup>:

<b>H<sup>a,b</sup></b> : 99PN, 97BK, 97DB, 96SI, 93SM, 90B, 87SA, 87SH, 86AH, 84VK, 80MR, 74NG, 67CC, 67CR, 67H	<b>Cr<sup>3+</sup></b> : 99DP	<b>Y<sup>3+</sup></b> : 91SK, 88BK, 79TK
<b>Mg<sup>2+</sup></b> : 93SM, 87SA, 87VO <sup>c</sup> , 74NA, 67CC	<b>Mn<sup>2+</sup></b> : 89SA, 88NK, 75MN	<b>La<sup>3+</sup></b> : 91SK, 88MK
<b>Ca<sup>2+</sup></b> : 97DB, 93SM, 88VO, 87SA, 74NA, 67CC, 67H	<b>Fe<sup>2+</sup></b> : 98FH, 97DB, 89SA, 87SH, 87PL	<b>Pr<sup>3+</sup></b> : 91SK, 88MK
<b>Sr<sup>2+</sup></b> : 93SM, 88VZ, 87SA, 74NA	<b>Fe<sup>3+</sup></b> : 87PL, 82KG, 67H	<b>Nd<sup>3+</sup></b> : 91SK, 88MK
<b>Ba<sup>2+</sup></b> : 93SM, 88VZ, 87SA, 74NA	<b>Co<sup>2+</sup></b> : 75MN	<b>Sm<sup>3+</sup></b> : 91SK, 88MK
<b>Ge(IV)</b> : 86SB, 84SB	<b>Ni<sup>2+</sup></b> : 99VO, 97DB, 90VS, 89SA, 86SA, 75MN, 67H	<b>Gd<sup>3+</sup></b> : 91SK, 88MK
<b>Pb<sup>2+</sup></b> : 97DB <sup>c</sup> , 88NK, 87SH	<b>Cu<sup>2+</sup></b> : 97BK, 97DB, 89SA, 88MK, 87SH, 86SA, 75MN	<b>Eu<sup>3+</sup></b> : 91SK, 88MK
<b>In<sup>3+</sup></b> : 79EF <sup>d</sup>	<b>Au<sup>3+</sup></b> : 86GF <sup>d</sup> , 86GS <sup>d</sup> , 85GS <sup>d</sup>	<b>Tb<sup>3+</sup></b> : 91SK, 88MK
<b>V(V)</b> : 82SP	<b>Zn<sup>2+</sup></b> : 97DB, 90VO <sup>c</sup> , 89SA, 88VS, 87SH, 75NM	<b>Dy<sup>3+</sup></b> : 91SK, 88MK
	<b>Cd<sup>2+</sup></b> : 97DB, 89SA, 88NK, 87SH, 78MZ, 75MN	<b>Ho<sup>3+</sup></b> : 91SK, 88MK
	<b>Sc<sup>3+c</sup></b> : 91SK	<b>Er<sup>3+</sup></b> : 91SK, 88MK
		<b>Tm<sup>3+</sup></b> : 91SK, 88MK
		<b>Yb<sup>3+</sup></b> : 91SK, 88MK
		<b>Lu<sup>3+</sup></b> : 91SK, 88MK
		<b>Th<sup>4+</sup></b> : 67H

*Experimental conditions:* $I = 3.4 \text{ M } (\text{CH}_4)_3\text{NCl}$ , 24 °C, NMR, Conc.: 99PN $I = 0.1 \text{ M KNO}_3$ , 25 °C, gl, Conc.: 97DB, 89SA, 87SA $I = 0.2 \text{ M KCl}$ , 25 °C, gl, Conc.: 97BK**Table 9** Recommended and provisional data for NTPH, 25 °C.

Cation	Equilibrium	$I/M$	$\lg K$	Category	References	
$\text{H}^+$	L + H	3.4 (Me <sub>4</sub> N)	14.2 (0.2)	P	99PN	
	HL + H	0.1 (K)	7.25 (0.05)	R	97DB, 87SA	
		0.2 (K)	6.98 (0.02)	P	97BK	
	$\text{H}_2\text{L} + \text{H}$	0.1 (K)	5.90 (0.02)	R	97DB, 87SA	
		0.2 (K)	5.69 (0.02)	P	97BK	
	$\text{H}_3\text{L} + \text{H}$	0.1 (K)	4.62 (0.05)	P	97DB, 87SA	
		0.2 (K)	4.46 (0.02)	P	97BK	
	$\text{Mg}^{2+}$	$\text{H}_4\text{L} + \text{H}$	0.2 (K)	1.5 (0.1)	P	97DB, 87SA
		M + HL	0.1 (K)	4.3 (0.2)	P	87SA
		ML + H	0.1 (K)	9.42 (0.04)	P	87SA
MHL + H		0.1 (K)	6.10 (0.04)	P	87SA	
$\text{MH}_2\text{L} + \text{H}$		0.1 (K)	4.8 (0.1)	P	87SA	
$\text{Ca}^{2+}$	M + HL	0.1 (K)	4.0 (0.2)	P	97DB, 87SA	
	ML + H	0.1 (K)	8.85 (0.05)	R	97DB, 87SA	
	MHL + H	0.1 (K)	6.2 (0.1)	P	97DB, 87SA	
	$\text{MH}_2\text{L} + \text{H}$	0.1 (K)	5.0 (0.1)	P	97DB, 87SA	
$\text{Sr}^{2+}$	$\text{MH}_3\text{L} + \text{H}$	0.1 (K)	4.1 (0.1)	P	97DB	
	M + HL	0.1 (K)	3.2 (0.2)	P	87SA	
	ML + H	0.1 (K)	9.40 (0.05)	P	87SA	
	MHL + H	0.1 (K)	6.15 (0.05)	P	87SA	
$\text{Ba}^{2+}$	$\text{MH}_2\text{L} + \text{H}$	0.1 (K)	5.0 (0.1)	P	87SA	
	M + HL	0.1 (K)	3.4 (0.2)	P	87SA	
	ML + H	0.1 (K)	9.70 (0.05)	P	87SA	
	MHL + H	0.1 (K)	6.20 (0.05)	P	87SA	
$\text{Mn}^{2+}$	$\text{MH}_2\text{L} + \text{H}$	0.1 (K)	5.1 (0.1)	P	87SA	
	M + HL	0.1 (K)	5.6 (0.2)	P	89SA	
	ML + H	0.1 (K)	7.37 (0.05)	P	89SA	
	MHL + H	0.1 (K)	5.93 (0.05)	P	89SA	
$\text{Fe}^{2+}$	$\text{MH}_2\text{L} + \text{H}$	0.1 (K)	4.7 (0.1)	P	89SA	
	M + HL	0.1 (K)	7.3 (0.2)	P	89SA	
	ML + H	0.1 (K)	6.45 (0.05)	R	97DB, 89SA	
	MHL + H	0.1 (K)	5.40 (0.05)	P	89SA	
$\text{Co}^{2+}$	$\text{MH}_2\text{L} + \text{H}$	0.1 (K)	4.2 (0.1)	P	89SA	
	M + HL	0.1 (K)	7.5 (0.2)	P	89SA	
	ML + H	0.1 (K)	6.3 (0.1)	P	89SA	
	MHL + H	0.1 (K)	5.10 (0.04)	P	89SA	
$\text{Ni}^{2+}$	$\text{MH}_2\text{L} + \text{H}$	0.1 (K)	3.6 (0.1)	P	89SA	
	M + HL	0.1 (K)	7.1 (0.2)	P	97DB, 89SA	
	ML + H	0.1 (K)	8.2 (0.1)	P	97DB, 89SA	
	MHL + H	0.1 (K)	5.60 (0.05)	R	97DB, 89SA	
$\text{Cu}^{2+}$	$\text{MH}_2\text{L} + \text{H}$	0.1 (K)	3.5 (0.1)	P	97DB, 89SA	
	M + HL	0.1 (K)	10.7 (0.2)	P	89SA	
		0.2 (K)	10.1 (0.2)	P	97BK	

*(Continued on next page)*

**Table 9** (Continued)

Cation	Equilibrium	<i>I/M</i>	lg <i>K</i>	Category	References
Zn <sup>2+</sup>	ML + H	0.1 (K)	6.34 (0.04)	R	97DB, 89SA
		0.2 (K)	6.18 (0.02)	P	97BK
	MHL + H	0.1 (K)	4.55 (0.05)	R	97DB, 89SA
		0.2 (K)	4.47 (0.02)	P	97BK
	MH <sub>2</sub> L + H	0.1 (K)	3.50 (0.05)	R	97DB, 89SA
		0.2 (K)	3.39 (0.05)	P	97BK
Cd <sup>2+</sup>	M + HL	0.1 (K)	8.2 (0.1)	P	89SA
	ML + H	0.1 (K)	6.2 (0.1)	P	97DB, 89SA
	MHL + H	0.1 (K)	5.0 (0.1)	P	97DB, 89SA
	MH <sub>2</sub> L + H	0.1 (K)	4.0 (0.1)	P	97DB, 89SA
Cd <sup>2+</sup>	M + HL	0.1 (K)	6.4 (0.2)	P	89SA
	ML + H	0.1 (K)	7.15 (0.04)	R	97DB, 89SA
	MHL + H	0.1 (K)	5.72 (0.04)	R	97DB, 89SA
	MH <sub>2</sub> L + H	0.1 (K)	4.1 (0.1)	P	97DB, 89SA

<sup>a</sup>[99PN]: 24 °C. The value lg*K*<sub>1</sub> = 14.2 [99PN] given as Provisional may not be well compatible with the medium used for the K(M + HL) measurement.

<sup>b</sup>All the potentiometric values reported for lg*K*<sub>1</sub>: 12.8 [93SM, 87SA], 12.5 [97DB], 12.3 [97BK], 12.1 [74NG], and 10.9 [67H] seem to be an underestimate. This conclusion is supported by an independent calorimetric evaluation at *I* → 0 (lg*K*<sub>1</sub> ~ 14) [84VK] and NMR results [99PN, 80MR]. An underestimation of lg*K*<sub>1</sub> leads to a corresponding error (decrease) in lg*K*<sub>ML</sub>. Thus, all the published lg*K*<sub>ML</sub> values are expected to have some systematic errors arising from this source. This is not the case for the M + HL equilibrium, given in Table 9. The reader must use discretion in attempting to effect full speciation calculation at pH >11 even with most reliable value among published ones: lg*K*<sub>1</sub> = 12.8 [87SA].

<sup>c</sup>[99VO, 90VO, 87VO]: only thermochemical data.

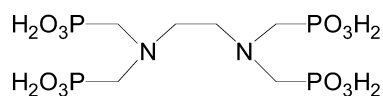
<sup>d</sup>[86GF, 86GS, 85GS, 79EF]: ternary complexes only.

<sup>e</sup>lg*K*(Pb + HL) = 10.0 (0.5); lg*K*(PbL + H) = 6.7 (0.1), *I* = 0.1 M KNO<sub>3</sub>, 25 °C, gl, Conc. [97DB].

<sup>f</sup>The higher protonated complexes M(III,IV)H<sub>*n*</sub>L (*n* > 2) are sparingly soluble, which makes the potentiometric investigations of lanthanide, iron(III), aluminium(III), thorium(IV), etc. complexes impossible. For Group IIIB elements and Lanthanoids, the following protonation constants reported by [91SK] (*I* = 0.1 M KNO<sub>3</sub>, 25 °C) could be accepted as **Provisional**:

M	lg <i>K</i> (ML + H)	lg <i>K</i> (MHL + H)	M	lg <i>K</i> (ML + H)	lg <i>K</i> (MHL + H)
Sc <sup>3+</sup>	7.12 (0.02)		Tb <sup>3+</sup>	7.34 (0.02)	5.48 (0.06)
Y <sup>3+</sup>	7.15 (0.02)	5.50 (0.06)	Dy <sup>3+</sup>	7.31 (0.02)	5.56 (0.06)
La <sup>3+</sup>	7.82 (0.02)	5.66 (0.06)	Ho <sup>3+</sup>	7.16 (0.02)	5.42 (0.06)
Pr <sup>3+</sup>	7.74 (0.02)	5.65 (0.06)	Er <sup>3+</sup>	6.98 (0.02)	5.5 (0.1)
Nd <sup>3+</sup>	7.52 (0.02)	5.50 (0.06)	Tm <sup>3+</sup>	7.01 (0.02)	5.6 (0.1)
Sm <sup>3+</sup>	7.49 (0.02)	5.36 (0.06)	Yb <sup>3+</sup>	7.02 (0.06)	
Eu <sup>3+</sup>	7.51 (0.02)	5.45 (0.06)	Lu <sup>3+</sup>	6.90 (0.02)	
Gd <sup>3+</sup>	7.37 (0.02)	5.34 (0.06)			

### 13. 1,2-DIAMINOETHANE-*N,N,N',N'*-TETRAKIS(METHYLENPHOSPHONIC ACID), EDTPH



Common names: DEQUEST 2041 (Monsanto)

The known synthetic methods for EDTPH preparation [67KD, 71MM] are susceptible to lesser-substituted by-products that are extremely difficult to remove [76MM]. The data published before 1976, according to [76MM], are of variable accuracy, depending on ligand purity. Thus, any report on EDTPH without an indication of the degree of purity must be treated with caution. At least the fact that the NMR-detectable impurities in EDTPH samples are “negligible” should be reported [77MR].

*Cations studied*<sup>a-f</sup>:

<b>H<sup>+</sup></b> : 99PN <sup>b</sup> , 98WM, 95JW <sup>c</sup> , 93SM, 91SK, 90B, 84RV, 81LY, 80MM, 79RZ, 78KP, 77MR, 76MM, 74KP, 71MM, 67KD, 65UA, 65WR, 56WM	<b>Mn<sup>2+</sup></b> : 67KD, 65WR, 56WM <b>Mn<sup>3+</sup></b> : 74KP <b>Fe<sup>3+</sup></b> : 87RA, 65WR, 56WM <b>Co<sup>2+</sup></b> : 95JW <sup>c</sup> , 76MM, 67KD <b>Ni<sup>2+</sup></b> : 95JW <sup>c</sup> , 76MM, 67KD <b>Cu<sup>2+</sup></b> : 95JW <sup>c</sup> , 80ZR, 76MM, 67KD, 65WR, 56WM <b>Zn<sup>2+</sup></b> : 95JW <sup>c</sup> , 76MM, 67KD <b>Cd<sup>2+</sup></b> : 80RA, 85KD, 79RZ, 67KD <b>Sc<sup>3+</sup></b> : 91SK <b>Y<sup>3+</sup></b> : 98WM, 91SK, 88MK, 71KS, 70T <b>La<sup>3+</sup></b> : 95JW <sup>c</sup> , 91SK, 88MK, 67KD <b>Ce<sup>3+</sup></b> : 72S, 71KS, 71S, 70T <b>Pr<sup>3+</sup></b> : 91SK, 88MK	<b>Nd<sup>3+</sup></b> : 91SK, 88MK, 67KD <b>Sm<sup>3+</sup></b> : 96WM, 95JW, 95WJ, 91SK, 67KD <b>Eu<sup>3+</sup></b> : 91SK, 88MK <b>Gd<sup>3+</sup></b> : 95WJ, 91SK, 67KD <b>Tb<sup>3+</sup></b> : 91SK, 88MK <b>Dy<sup>3+</sup></b> : 91SK, 88MK <b>Ho<sup>3+</sup></b> : 95JW, 95WJ, 91SK, 67KD <b>Er<sup>3+</sup></b> : 91SK, 88MK <b>Tm<sup>3+</sup></b> : 91SK, 67KD <b>Yb<sup>3+</sup></b> : 95JW <sup>c</sup> , 91SK, 88MK <b>Lu<sup>3+</sup></b> : 91SK, 88MK <b>Am<sup>3+</sup></b> : 72S, 71S <b>Cm<sup>3+</sup></b> : 72S, 71S
<b>Mg<sup>2+</sup></b> : 95JW <sup>c</sup> , 93SM, 80RA, 79RZ, 76MM, 67KD <b>Ca<sup>2+</sup></b> : 95JW, 93SM, 80RA, 79RZ, 76MM, 70T, 67KD, 65WR, 56WM <b>Sr<sup>2+</sup></b> : 93SM, 79RZ, 70T <b>Ba<sup>2+</sup></b> : 93SM, 80RA, 79RZ <b>Ga<sup>3+</sup></b> : 85KV, 83KD, 80MM <b>In<sup>3+</sup></b> : 83KD <b>Tl<sup>3+</sup></b> : 74KP <b>Ge(IV)</b> : 86SB, 83SZ <b>V(V)</b> : 82SP		

*Experimental conditions:*

*I* = 3.5 M (CH<sub>4</sub>)<sub>3</sub>NCl, 24 °C, NMR, Conc.: 99PN

*I* = 0.1 M KNO<sub>3</sub>, 25 °C, gl, Conc.: 93SM, 91SK, 76MM

**Table 10** Recommended and provisional data for EDTPH, 25 °C.

Cation	Equilibrium	<i>I</i> / <i>M</i>	lg <i>K</i>	Category	References
H <sup>+</sup>	L + H	3.5 (Me <sub>4</sub> N)	13.8 (0.1)	P <sup>b</sup>	99PN
	HL + H	0.1 (K)	9.82 (0.04)	R	93SM, 76MM
	H <sub>2</sub> L + H	0.1 (K)	7.90 (0.04)	R	93SM, 76MM
	H <sub>3</sub> L + H	0.1 (K)	6.40 (0.02)	R	93SM, 76MM
	H <sub>4</sub> L + H	0.1 (K)	5.12 (0.02)	R	93SM, 76MM
	H <sub>5</sub> L + H	0.1 (K)	3.00 (0.04)	R	93SM, 76MM
Mg <sup>2+</sup>	H <sub>6</sub> L + H	0.1 (K)	1.3 (0.1)	P	93SM, 76MM
	M + HL	0.1 (K)	5.40 (0.05)	R	93SM, 76MM
	ML + H	0.1 (K)	10.00 (0.05)	R	93SM, 76MM
	MHL + H	0.1 (K)	8.76 (0.05)	R	93SM, 76MM
	MH <sub>2</sub> L + H	0.1 (K)	6.91 (0.05)	R	93SM, 76MM
	MH <sub>3</sub> L + H	0.1 (K)	5.2 (0.2)	P	93SM, 76MM
Ca <sup>2+</sup>	M + HL	0.1 (K)	5.75 (0.05)	R	93SM, 76MM
	ML + H	0.1 (K)	9.44 (0.05)	R	93SM, 76MM
	MHL + H	0.1 (K)	8.3 (0.1)	P	93SM, 76MM
	MH <sub>2</sub> L + H	0.1 (K)	6.65 (0.05)	R	93SM, 76MM

(Continued on next page)

Table 10 (Continued)

Cation	Equilibrium	<i>I/M</i>	lg <i>K</i>	Category	References
Sr <sup>2+</sup>	MH <sub>3</sub> L + H	0.1 (K)	5.2 (0.1)	P	93SM, 76MM
	M + HL	0.1 (K)	4.6 (0.2)	P	93SM
	ML + H	0.1 (K)	10.10 (0.05)	P	93SM
	MHL + H	0.1 (K)	8.50 (0.05)	P	93SM
	MH <sub>2</sub> L + H	0.1 (K)	6.90 (0.05)	P	93SM
Ba <sup>2+</sup>	MH <sub>3</sub> L + H	0.1 (K)	5.4 (0.1)	P	93SM
	M + HL	0.1 (K)	4.4 (0.2)	P	93SM
	ML + H	0.1 (K)	10.30 (0.05)	P	93SM
	MHL + H	0.1 (K)	8.50 (0.05)	P	93SM
	MH <sub>2</sub> L + H	0.1 (K)	7.10 (0.05)	P	93SM
Co <sup>2+</sup>	MH <sub>3</sub> L + H	0.1 (K)	5.8 (0.1)	P	93SM
	M + HL	0.1 (K)	12.4 (0.1)	P	76MM
	ML + H	0.1 (K)	8.30 (0.05)	P	76MM
	MHL + H	0.1 (K)	6.50 (0.05)	P	76MM
	MH <sub>2</sub> L + H	0.1 (K)	5.30 (0.05)	P	76MM
Ni <sup>2+</sup>	MH <sub>3</sub> L + H	0.1 (K)	4.3 (0.1)	P	76MM
	M + HL	0.1 (K)	12.3 (0.1)	P	76MM
	ML + H	0.1 (K)	8.90 (0.05)	P	76MM
	MHL + H	0.1 (K)	7.40 (0.05)	P	76MM
	MH <sub>2</sub> L + H	0.1 (K)	5.50 (0.05)	P	76MM
Cu <sup>2+</sup>	MH <sub>3</sub> L + H	0.1 (K)	4.3 (0.1)	P	76MM
	M + HL	0.1 (K)	17.8 (0.1)	P	76MM
	ML + H	0.1 (K)	7.60 (0.05)	P	76MM
	MHL + H	0.1 (K)	6.00 (0.05)	P	76MM
	MH <sub>2</sub> L + H	0.1 (K)	4.60 (0.05)	P	76MM
Zn <sup>2+</sup>	MH <sub>3</sub> L + H	0.1 (K)	3.7 (0.1)	P	76MM
	M + HL	0.1 (K)	14.1 (0.1)	P	76MM
	ML + H	0.1 (K)	8.30 (0.05)	P	76MM
	MHL + H	0.1 (K)	6.10 (0.05)	P	76MM
	MH <sub>2</sub> L + H	0.1 (K)	5.00 (0.05)	P	76MM
	MH <sub>3</sub> L + H	0.1 (K)	3.1 (0.1)	P	76MM

<sup>a</sup>EDTPH has a zwitter-ionic structure with a “chelated” proton in both aqueous and solid states [90SP]. It is characterized by 10, mostly overlapping, protonation-dissociation steps which span a much broader pH range than the usual acid-base titration with a glass electrode can identify [89BN]. The pH-metric titrations used in most publications are therefore inadequate to characterize lg*K*<sub>1</sub> and lg*K*<sub>7</sub>, lg*K*<sub>8</sub>, lg*K*<sub>9</sub>, and lg*K*<sub>10</sub> values or to establish the purity of this chelating agent. The highest lg*K*<sub>1</sub> values derived from potentiometry in 0.1 M KNO<sub>3</sub> are 13.0 [93SM] and 13.14 [71MM] for *I* = 0.1 and 25 °C. Both still seem to be underestimates. Although the authors of [93SM] report that their evaluation is also supported by NMR, the corresponding data are missing.

<sup>b</sup>[99PN]: 24 °C, The value lg*K*<sub>1</sub> = 13.8 [99PN] given as Provisional may not be compatible with the medium used for the *K*(M + HL) measurement and a certain discretion is required in attempting to effect a full speciation calculation at pH >11.

<sup>c</sup>[95JW] used the experimental conditions: gl, Conc. *I* = 0.15 NaCl, 37 °C.

<sup>d</sup>Complexation of Gallium(III) [85KV, 83KD, 80MM] is complicated by poor solubility of the protonated species at the beginning of the potentiometric titration (pH <2.9). [80MM] proposed to calculate lg*K*<sub>ML</sub> from the competition reaction and the “well-known” constants for Ga(III) hydrolysis: GaL<sup>5-</sup> + 4OH<sup>-</sup> = Ga(OH)<sub>4</sub><sup>-</sup> + L<sup>8-</sup>. The accuracy of data published by [80MM] is therefore strongly dependent on the validity of corresponding stability constants of Ga(OH)<sub>4</sub><sup>-</sup>. The value lg *K*(Ga + HL) = 25(1) (25 °C, *I* = 0.1 M KNO<sub>3</sub>, gl, Conc.) clearly indicates a high affinity of EDTPH towards Ga(III).

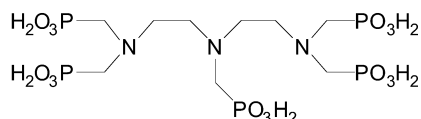
<sup>e</sup>Within the range 6 <pH <10 Yttrium(III) and M(III) of 4,5/*f*-elements [95WJ, 91SK, 72S, 67KD, 71S, 71KS, 70T] form soluble, stable ML and MH<sub>*n*</sub>L complexes. Like iron(III) they give poorly soluble protonated compounds at pH <5. This causes a serious problem for the potentiometric method [91SK]. The

data, derived from generally less accurate methods: ion electromigration [72S, 71S] and ion exchange [71KS], with trace concentration levels of M(III), are free from the problems of low solubility and are in satisfactory agreement. The values  $\lg K(\text{Ce} + \text{HL}) = 17.5 (0.5)$ ;  $\lg K(\text{Am} + \text{HL}) = 18.5 (0.5)$ ;  $\lg K(\text{Cm} + \text{HL}) = 17.7 (0.5)$  (25 °C,  $I = 0.1 \text{ M KNO}_3$ , Mix.) could thus be included as reliable.

<sup>f</sup>The protonation constants  $\lg K(\text{LnL} + \text{H})$ , given in [91SK] ( $I = 0.1 \text{ M KNO}_3$ , 25 °C, gl) could be accepted as **Provisional**:

M	$\lg K(\text{ML} + \text{H})$	$\lg K(\text{MHL} + \text{H})$	M	$\lg K(\text{ML} + \text{H})$	$\lg K(\text{MHL} + \text{H})$
Sc <sup>3+</sup>	7.0 (0.1)	8.1 (0.1)	Tb <sup>3+</sup>	7.41 (0.02)	6.14 (0.02)
Y <sup>3+</sup>	7.17 (0.02)	5.9 (0.1)	Dy <sup>3+</sup>	7.36 (0.02)	6.07 (0.02)
La <sup>3+</sup>	7.1 (0.1)	7.6 (0.1)	Ho <sup>3+</sup>	7.32 (0.02)	6.07 (0.02)
Pr <sup>3+</sup>	7.17 (0.02)	6.88 (0.02)	Er <sup>3+</sup>	7.36 (0.02)	6.1 (0.1)
Nd <sup>3+</sup>	7.19 (0.02)	6.68 (0.02)	Tm <sup>3+</sup>	7.29 (0.02)	6.0 (0.1)
Sm <sup>3+</sup>	7.34 (0.02)	6.29 (0.02)	Yb <sup>3+</sup>	7.24 (0.02)	5.8 (0.1)
Eu <sup>3+</sup>	7.31 (0.02)	6.25 (0.02)	Lu <sup>3+</sup>	7.42 (0.02)	5.9 (0.1)
Gd <sup>3+</sup>	7.35 (0.02)	6.19 (0.02)			

#### 14. DIETHYLENTRIAMINE-*N,N,N',N',N''*-PENTAKIS(METHYLENPHOSPHONIC ACID), DTPPH



*Common name*: DEQUEST 2060 (Monsanto)

The metal scavenging ability of DTPPH seems to be the highest among the organophosphonates. The absence of any precipitation of 1:1 complexes over a wide pH range,  $0 < \text{pH} < 14$ , gives DTPPH a great advantage over other organophosphonates (EDTPH, NTPH, HEDPA) [92H, 89GH]. However, the number of stability constants published for this ligand is surprisingly small:  $\text{H}^+$  [67KD, 68T, 84ZG, 87ZG], alkaline earths [84ZG, 67KD, 68T], *3d*-elements [67KD, 84ZG],  $\text{Cd}^{2+}$ , [67KD],  $\text{Ga}^{3+}$  [85KV], Ge(IV) [84SB], V(V) [82SP], rare earths [68T, 79ZK, 84ZG, 87ZG], and U(VI) [79ZK].

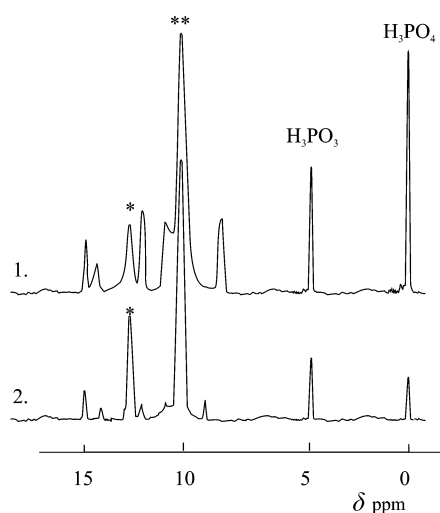
This fact can be attributed in part to significant difficulties with the ligand's synthesis and purification. Normally the dominating "impurity" is an under-phosphorylated derivative with a methyl group in place of one of the terminal methylene-phosphonate groups [89GN]. Besides substantial amounts of under-phosphorylated amines, the DTPPH samples generally contain "free"  $\text{H}_3\text{PO}_3/\text{H}_3\text{PO}_4$ .

Most of the data published [67KD, 68T, 79MZ, 79ZK, 82SP, 84SB, 85KV], are based on IREA samples. We have examined several samples of solid DTPPH from IREA, dated 1980–1994, by NMR, Fig. 2. This analysis revealed only 60–75% DTPPH content. At the same time, the element analysis data for the same white powder samples was well consistent with the chemical composition of DTPPH, which was not surprising taking into account that the impurities are a mixture of the under-phosphorylated derivative and "free"  $\text{H}_3\text{PO}_3/\text{H}_3\text{PO}_4$ .

The element analyses used in 1960–1970 have normally been unable to detect these impurities even though present at up to 50%. Taking into account the large number of protons in the DTPPH system, the direct acid-base titration also is inadequate to indicate the degree of purity in this case. We therefore treat the communications that did not pass NMR control [67KD, 68T, 79MZ, 82SP, 84SB, 85KV], as well as some others that do not report any analysis at all [87ZG, 84ZG], as doubtful and reject the corresponding values.

The best DTPPH powder sample reported recently [89GH] had a 93% purity (according to NMR). The  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR titration of DTPPH covered the pH range 1–14, but even at pH 14 the deprotonation of the ligand was evidently incomplete. The  $\lg K_1$  value is therefore much higher than those reported by [67KD, 68T] and can be estimated as ~13–15. This result supports indirectly the  $\lg K_1$  data of [99PN, 77MR, 80MR] for NTPH and EDTPH.





**Fig. 2**  $^{31}\text{P}$  (H-decoupled) NMR spectra of DTPPH solid samples dissolved in  $\text{D}_2\text{O}$ . 1. Typical white powder sample of IREA, 1989. 2. Solid sample from Monsanto, 1985. Symbols indicate central (\*) and terminal (\*\*) phosphonic groups of DTPPH

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## 16. APPENDIX: DISCUSSION AND CONCLUDING REMARKS

The simplest organophosphonate, methylphosphonic acid, reveals higher ML complex stability than does acetic acid (by about one order of magnitude) for both alkaline earth and 3d-metal ions. This fact demonstrates the almost equal importance for coordination compound stability of an increase in ligand basicity and an increase in number of ionic and covalent bonds. Within the 3d-elements definite but small deviations from the Irving–Williams sequence can be seen: Cu > Mn > Co ~ Ni. Although the systematic error is higher than some of the differences in  $\lg K_{ML}$ , the relative error is expected to be small enough to make this a valid conclusion.

Bisphosphonates have significantly higher stability constants than those of monodentate alkylphosphonic acids owing to both higher basicity and bidentate coordination. The  $\lg K_{ML}$  values for HEDPA and CMDPA are also much higher than those for the dicarboxy analog malonic acid. For the pair HEDPA/CMDPA, there is a reasonable difference in stability that can be attributed to the electron-attracting effect of the two Cl-atoms.

Aminomethylenephosphonic acids (AMPH, IDPH, MIDPH, NTPH) also demonstrate generally higher affinity to cations than their carboxy analogs, Table 11.

According to the NMR data, NTPH, like NTA, forms  $H_7L^+$  species [80MR]. The corresponding constants have yet to be determined. The same situation applies to the  $H_9L^+$  and  $H_{10}L^{2+}$  species of EDTPH [77MR]. These constants must be taken into account to achieve higher accuracy for  $M + H_nL \leftrightarrow MH_nL$  ( $n = 5-6$  for NTPH and 7–8 for EDTPH) stability constants measured in highly acidic media.

**Table 11** Stability constants ( $\lg K_{ML}$ ) of aminomethylenephosphonates and their carboxy-analogs ( $I = 0.1$  M, 25 °C)<sup>a-d</sup>.

M	AMPH	Gly [91KS]	MIDPH	MIDA [65A] <sup>d</sup>	NTPH <sup>a,b,c</sup>		NTA [82A]	EDTPH <sup>a,b,c</sup>		EDTA [77A]
H <sup>+</sup>	10.07	9.60	12.1	9.65	14.2 <sup>a</sup>	12.7 <sup>b</sup>	9.7	13.8 <sup>a</sup>	13.0 <sup>b</sup>	10.26
Mg <sup>2+</sup>	1.99	–	5.1	3.44	9.0 <sup>c</sup>	7.5 <sup>b</sup>	5.43	9.1 <sup>c</sup>	8.4 <sup>b</sup>	8.69
	1.67	–	4.6	3.75	9.4 <sup>c</sup>	7.9 <sup>b</sup>	6.45	10.1 <sup>c</sup>	9.4 <sup>b</sup>	10.7
Ca <sup>2+</sup>	1.34	–	4.0	2.85	8.0 <sup>c</sup>	6.5 <sup>b</sup>	5.0	8.3 <sup>c</sup>	7.6 <sup>b</sup>	8.6
	4.5	4.66	9.4	7.62	15.5 <sup>c</sup>	14.0 <sup>b</sup>	10.4	17.8 <sup>c</sup>	17.1 <sup>b</sup>	16.11
Sr <sup>2+</sup>	5.3	5.8	9.5	8.73	13.2 <sup>c</sup>	11.7 <sup>b</sup>	11.5	17.1 <sup>c</sup>	16.4 <sup>b</sup>	18.6
Co <sup>2+</sup>	8.10	8.2	14.2	11.09	18.7 <sup>c</sup>	17.2 <sup>b</sup>	13.0	23.9 <sup>c</sup>	23.2 <sup>b</sup>	18.8
	–	5.0	10.2	7.66	16.1 <sup>c</sup>	14.6 <sup>b</sup>	10.7	19.5 <sup>c</sup>	18.8 <sup>b</sup>	16.26
Ni <sup>2+</sup>										
Cu <sup>2+</sup>										
Zn <sup>2+</sup>										

<sup>a</sup>Data obtained by NMR ( $I = 3.4-3.5$  M Me<sub>4</sub>NCl; 24 °C [99PN]).

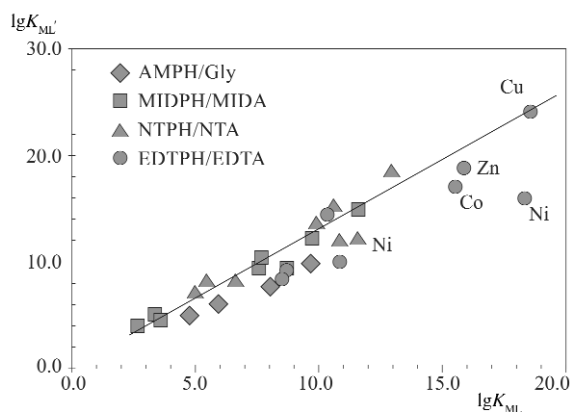
<sup>b</sup> $\lg K_{ML}$ : obtained by potentiometry. The values are averaged from the most reliable published data [93SM, 89SA, 87SA, 76MM].

<sup>c</sup> $\lg K_{ML}^{corr}$  are derived from recalculation of  $\lg K_{ML}$  using NMR-estimated  $\lg K_1$ -values, e.g., for EDTPH  $\lg K_1 = 13.8$  [99PN], instead of the value 13.14 [71MM].

<sup>d</sup>Data for 20 °C.

An NMR-estimated difference in  $\lg K_1$  for NTPH ( $\lg K_1 = 14.2$ ) and EDTPH ( $\lg K_1 = 13.8$ ) under comparable conditions (3.4–3.5 M  $(CH_3)_4NCl$ , 24 °C [99PN]) is an unexpected result. EDTPH<sup>8-</sup> demonstrates lower affinity towards  $H^+$  than NTPH<sup>6-</sup> although the formal negative charge of EDTPH is higher. This fact is in disagreement with the corresponding one for NTA ( $\lg K_1 = 9.7$ ) and EDTA ( $\lg K_1 = 10.26$ ) [77A, 82A]. The higher affinity of NTPH toward protons than that of EDTPH could be due to the inability of the latter to simultaneously arrange the equal number of phosphonate groups for a proton chelation.

Corrected  $\lg K_{ML}$  values for NTPH (Table 11) give a good linear correlation with IUPAC recommended data for NTA (see Fig. 3). The slope clearly indicates that ML complexes of NTPH generally have higher stability than those of NTA. This conclusion is indirectly supported by numerous reports of higher resistance of NTPH complexes to decomposition due to hydrolysis (competition of  $HO^-$  ions for M) and protonation (competition of protons for L) than those of NTA. The linear relationship between NTPH and NTA stability constants also reflects the structural uniformity of changes that take place when a carboxy-group is substituted by a phosphonic one. The domination of NTPH-complex stability over those for NTA complexes can therefore be attributed to the electrostatic changes occurring within approximately the same structure that involves tetradentate ligands in both cases. The only significant exception is represented by  $Ni^{2+}$  which forms uncharacteristically weak complexes with NTPH ( $\lg K_{ML}:Cu \gg Co > Ni$ ). This result has been reproduced in numerous independent publications. The same situation is evident for EDTPH. The Irving–Williams sequence does not, therefore, apply in these cases. The reasons are unclear. At the same time, this is not the case of AMPH and MIDPH. One of the possible explanations could be based on very slow equilibration of  $Ni^{2+}$  in comparison with  $Cu^{2+}$  and  $Co^{2+}$ . In the case of EDTPH, which is known to be the least kinetically flexible among the ligands under consideration, the stability sequence for ML complexes directly follows the rates of water molecule exchange in aqua-complexes of 3d-cations:  $Cu^{2+} > Zn^{2+} > Co^{2+} \gg Ni^{2+}$  [98M, 74W]. At the same time, the deviation from the Irving–Williams sequence for  $\lg K(M + HL)$  is not so pronounced as for ML. Thus, although higher organophosphonates are reported to reveal a clear departure from the



**Fig. 3** Free-energy correlations for organophosphonates ( $\lg K_{ML}'$ ) and their carboxy-analogs ( $\lg K_{ML}$ ). For NTPPH and EDTPH only  $\lg K_{ML}^{corr}$  values are used.

Irving–Williams sequence, this effect could be at least partly attributed to an insufficient equilibration time within the titration series.

The correlation with data for EDTA and NTA indicates that both NTPH and EDTPH should have non-zero stability constants with  $\text{Na}^+$  and  $\text{K}^+$ . For  $\text{K}^+$ , the  $\lg K_{\text{ML}}$  values are expected to be about 2–2.5 for EDTPH and 0.9–1.1 for NTPH. This conclusion is supported by some as yet unpublished results [90B]. The same observation was reported for alkali ion complexation of tetraazamacrocyclic methylenephosphonates [90DS]. All data published for  $\lg K_1$  and  $\lg K_2$  for both NTPH and EDTPH are for a  $\text{KNO}_3$  medium; therefore, they should be corrected for  $\text{K}^+$  complexation or re-evaluated in  $\text{R}_4\text{NCl}$  media. The same conclusion seems to be valid for AMPH, PMG, IDPH, and MIDPH.

For EDTPH/EDTA complexes with  $\text{H}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ce}^{3+}$ , and  $\text{Ga}^{3+}$ , a similar correlation to that with NTPH/NTA is observed. Moreover, the corresponding points correlate well with the pair NTPH/NTA. This probably indicates that the observed increase in stability occurs because of similar structures involving hexadentate ligands, which have the same electrostatic and conformational character as the NTPH/NTA pair. An increase of complex stability when an aminocarboxy ligand is substituted by its phosphonic analog seems therefore to be the general rule.

The speculation that mutual charge repulsion between phosphonate groups may increase the tendency for ML complexes to have uncoordinated ligand groups compared with the corresponding carboxylate analogs [85MM, 83OS, 71MM, 56WR] is not supported by most of the experimental data. The direct spectroscopic observations for  $[\text{Be}(\text{hedpa})_2]^{6-}$  by NMR [87GL] and for  $[\text{VO}(\text{H}_1\text{hedpa})_2]^{8-}$  by ESR [96SM] as well as crystal structure of  $\text{K}_6[\text{MoO}_2(\text{hedpa})_2] \cdot 12\text{H}_2\text{O}$  [93ST] and potentiometric evidence of highly stable *bis*-complex  $[\text{Cu}(\text{idph})_2]^{6-}$  formation [97BK], definitely refute this argument at least for the ML complexes of ligands that have up to four phosphonic groups (NTPH, EDTPH), or for corresponding *bis*-complexes (e.g.,  $[\text{M}(\text{idph})_2]^{x-}$ ).

For example, from spectroscopic observations, the  $\text{Ni}^{2+}$ -EDTPH complex [83OS] does not decompose at pH 11, whereas  $\text{Ni}^{2+}$ -EDTA is less stable. Taking into account the “low” affinity of phosphonates for  $\text{Ni}^{2+}$  the “true”  $\lg K_{\text{ML}}$  for Ni-EDTPH should probably be low compared with other 3*d*-metal ion complexes of EDTPH, but it is still higher than that for Ni-EDTA. The  $\lg K_{\text{ML}}^{\text{corr}}$  for  $\text{Ni}^{2+}$ -EDTPH seems therefore to be more realistic than the original value, although still an underestimate, Table 11.

Comparison of EDTPH data and the critically evaluated equilibrium data for EDTA with the cations  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ni}^{2+}$  demonstrates a lack of correlation. There is only a small increase in stability, if any, over EDTA (see Table 11). The Provisional critical data for EDTPH complexes with alkaline earth cations,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  seem therefore to be underestimates. Otherwise, it is not possible to justify numerous experimental observations of EDTPH efficiency in highly basic solutions (e.g., detergents) on the grounds of the existing compendium of stability constants.

At the same time, mutual electrostatic repulsion when the total electrostatic charge of donor groups exceeds eight units is likely to take place. This effect is probably responsible for the fact that in the Tl(III) *bis*-complex of glycine-*N,N*-bis(methylphosphonic acid),  $[\text{TlL}_2]^{7-}$ , one of the ligands has lower denticity than the other [98PA].

NTPH has some distinctive properties compared with its carboxy-analog, NTA. The organophosphonic ligand is less capable of forming *bis* complexes  $\text{ML}_2$ ; these are not observed for the alkaline earths, 3*d*-elements or aluminium ions [84LP]. They do exist for the rare earth cations and thallium (III), but less characteristically than with NTA [87GL].

The data presented above indicate clearly that potentiometry is not appropriate for estimating  $\lg K_1$  values for polydentate aminopolyalkylphosphonates (NTPH, EDTPH, DTPPH): almost all data published on  $\lg K_{\text{ML}}$  are therefore underestimates. At the same time, the recent use of NMR [97BL, 97CC, 96SI, 93SK, 93SM, 89SA, 86SA, 86AH, 83RC, 80MR, 77MR, 67CR] for these and related ligands also seems to be inadequate. None of the NMR research groups managed to reach the “plateau” where the chemical shift of the completely deprotonated ligand is independent of pH, nor to pass the half-neutralization point. Although some recent computer programs, e.g., Sigmaplot, WinEQNMR

could provide  $\lg K_1$  operating only with those chemical shifts that are below half-neutralization point, the accuracy of  $\lg K_1$  estimation becomes rather low.

Further, none of these groups used constant ionic strength at high pH or tried to demonstrate that the chemical shift is independent of ionic strength within this very high pH range. The chemical shifts are sensitive to deviations in  $(\text{CH}_3)_4\text{NCl}$  content [99PN, 95R] [associated mostly with the  $(\text{CH}_3)_4\text{N}^+$  cation]. Also, the possible influence the internal standard on the chemical equilibrium and the ionic strength should be specified. Unless this is done, the numerical data reported should be treated as rough estimations.

These concluding remarks are intended to be helpful in both methodological and theoretical aspects of data treatment in the very promising area of organophosphonic compounds aqueous equilibrium.