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ANALYTICAL CHEMISTRY DIVISION\*

# CRITICAL EVALUATION OF STABILITY CONSTANTS OF METAL COMPLEXES OF COMPLEXONES FOR BIOMEDICAL AND ENVIRONMENTAL APPLICATIONS\*\*

(IUPAC Technical Report)

Prepared for publication by

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# Critical evaluation of stability constants of metal complexes of complexones for biomedical and environmental applications

## (IUPAC Technical Report)

*Abstract:* Available experimental data on stability constants of proton (hydron) and metal complexes for seven complexones of particular biomedical and environmental interest: iminodiacetic acid (2,2'-azanediyl)diacetic acid, IDA); (methyl-imino)diacetic acid (2,2'-(methylazanediyl)diacetic acid, MIDA); 2,2',2'',2'''-[[[(carboxymethyl)azanediyl]bis[(ethane-1,2-diyl)nitrilo]]]tetraacetic acid (DTPA); 3,6,9,12-tetrakis(carboxymethyl)-3,6,9,12-tetraazatetradecanedioic acid (TTHA); 2,2',2''-(1,4,7-triazanonane-1,4,7-triyl)triacetic acid (NOTA); 2,2',2'',2'''-(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetraacetic acid (DOTA); 2,2',2'',2'''-(1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetrayl)tetraacetic acid (TETA), published in 1945–2000, have been critically evaluated. Some typical errors in stability constant measurements for particular complexones are summarized. Higher quality data are selected and presented as “**Recommended**” or “**Provisional**”.

*Keywords:* Complexones; proton complexes; metal complexes; stability constants; biomedical; environmental; Division V.

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## 1. INTRODUCTION

The name complexone was introduced in 1945 by G. Schwarzenbach [45SKa] for a series of artificial amino acids, containing normally at least one iminodiacetic acid group,  $N(\text{CH}_2\text{COOH})_2$ , or two aminoacetic acid groups,  $\text{NHCH}_2\text{COOH}$ . Two of these substances were already known at that time under the names Trilon A and B, and were used to eliminate hardness of water arising from calcium and magnesium ions without separating them from the water. Schwarzenbach demonstrated that, in solution, aminopolycarboxylate anions are able to bind calcium and other cations so strongly that they sometimes cannot be detected by the usual classical precipitation or colorimetric reagents. Further research indicated the capability of complexones to form stable highly soluble complexes with almost all known metal ions [05BC, 03IU, 88DT, 87AN].

The high values for the stability constants of the complexes formed by these ligands are due to the cumulative effect of basic amino groups and the high negative charge of several carboxylate groups, as well as the formation of numerous stable five-membered chelate rings with the metal ions. As the importance of critical assessment of stability constant data for complexones is widely recognized [87SM], two ligands [nitrilotriacetic acid (NTA) and 2,2',2'',2'''-(ethane-1,2-diyl)dinitrilo)tetraacetic acid, better known as ethylenediaminetetraacetic acid (EDTA,  $\text{H}_4\text{edta}$ )] have been reviewed previously within IUPAC Projects [82ANa, 77AA].

The present study involves evaluation of all reported proton (hydrogen ion, hydron; see first footnote, p. 1450) and metal ion binding constants for the remaining commonly used complexones, and the identification of recommended values for use in chemical speciation calculations. Within these objectives, a priority was given to compounds of strong medical and environmental importance and to those (IDA and MIDA) that represent complex-forming fragments and decomposition products of higher denticity complexones.

Within a broad variety of applications, complexones have in common the regulation of metal concentrations in widely differing systems. Uses of complexones span fields such as detergents, textile and paper processing, photographic developing solutions, scale solubilization in processing tanks, electroplating, control of the activity of metal-dependent polymerization, etc. [92HE, 88DT, 87AN]. The high solubility and stability of complexes formed by complexones make them useful as components of agricultural micro-fertilizers [88DT, 87AN]. Annual industrial output of EDTA and other complexones is in the thousands of tons [92HE].

Ligands considered		
IUPAC ligand name	Acronym	Other names <sup>d</sup>
Iminodiacetic acid <sup>b</sup>	IDA, H <sub>2</sub> ida	2,2'-Azanediyldiacetic acid <sup>b</sup> Iminodiethanoic acid <sup>c</sup>
(Methylimino)diacetic acid <sup>b</sup>	MIDA, H <sub>2</sub> mida	2,2'-(Methylazanediyldiacetic acid <sup>b</sup> (Methylimino)diethanoic acid <sup>c</sup>
2,2',2'',2'''-[[Carboxymethyl)azanediyldi]bis [(ethane-1,2-diy)nitri]l]tetraacetic acid <sup>b</sup>	DTPA, H <sub>5</sub> dtpa	Diethylenetriamine- <i>N,N,N',N'',N'''</i> -pentaacetic acid <sup>c</sup> ; Pentenic acid <sup>c</sup> ; Diethylenetriaminepentaethanoic acid <sup>d</sup> , <i>N,N</i> -bis[2-(bis[Carboxymethyl]amino)ethyl]glycine <sup>e</sup>
3,6,9,12-Tetrakis(carboxymethyl)-3,6,9,12-tetra- azatetradecanedioic acid <sup>b</sup>	TTHA, H <sub>6</sub> ttha	Triethylenetetramine- <i>N,N,N',N'',N'''</i> -hexaacetic acid <sup>c</sup> Triethylenetetraminehexaethanoic acid <sup>d</sup>
2,2',2''-(1,4,7-Triazanonane-1,4,7-triyl)triacetic acid <sup>b</sup>	NOTA, H <sub>3</sub> nota	1,4,7-Triazacyclononane-1,4,7-triacetic acid <sup>c</sup> 1,4,7-Triazacyclononane-1,4,7-triethanoic acid <sup>d</sup>
2,2',2'',2'''-(1,4,7,10-Tetraazacyclododecane- 1,4,7,10-tetrayl)tetraacetic acid <sup>b</sup>	DOTA, H <sub>4</sub> dota	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraethanoic acid <sup>d</sup>
2,2',2'',2'''-(1,4,8,11-Tetraazacyclotetradecane- 1,4,8,11-tetrayl)tetraacetic acid <sup>b</sup>	TETA, H <sub>4</sub> teta	1,4,8,11-Tetraazacyclotetradecane-1,4,8,11-tetraethanoic acid <sup>d</sup>

<sup>a</sup>In this report, the names that have been most frequently encountered in the literature are used.

<sup>b</sup>Names in accordance with IUPAC recommendations.

<sup>c</sup>Names used in IUPAC SC-Database [03IU] and in accordance with IUPAC nomenclature.

<sup>d</sup>Names used in IUPAC SC-Database [03IU] and not in accordance with IUPAC nomenclature.

<sup>e</sup>Name not recommended by IUPAC.

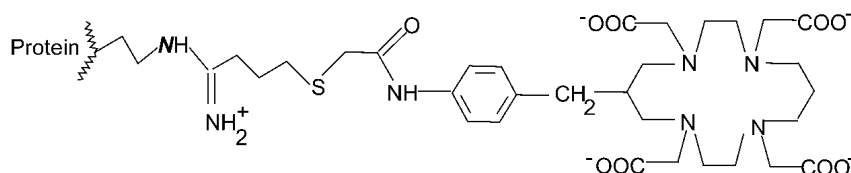
The highly stable complexes formed with polyaminopolycarboxylate ligands are of particular importance in biology and medicine [05BC, 01LE, 00BCa, 00HF, 98AB, 97BH, 84DMb]. The initial field of complexone biomedical application was chelation therapy [99CT]. Since the advent of nuclear fission during the 1940s, mankind has been increasingly exposed to the possibility of radionuclide intoxication from nuclear weapons testing and the expanding use of nuclear fission as a source of power. Only a small proportion of transuranic elements assimilated by humans is excreted, with the remaining part being retained, and the danger that continuing emission of radiation will eventually lead to tumor formation. Accordingly, efficient removal of radionuclides from the body by DTPA calcium complexes was proposed [88DT, 83MB]. The therapeutic antitumor use of radionuclides is based mostly on chelating agents. At the present time DTPA, as well as DOTA, NOTA, and their derivatives, are the agents of choice [01LE, 99AN, 99VH, 96SA, 90LT, 84DMb].

Another medical application where complexones are particularly important is magnetic resonance imaging (MRI). In MRI, paramagnetic metal complexes are used to increase image contrast [00BC, 99AW, 99CE, 98AB, 95AL]. The first clinically utilized contrast enhancement agent (MAGNEVIST) was based on the [Gd(dtpa)]<sup>2-</sup> complex, which distributes in extracellular space and significantly increases proton relaxation rates [98AB]. [Gd(dota)]<sup>-</sup> has also entered into clinical practice. Both of these complexes are now reference compounds for development and evaluation of new agents. Other paramagnetic lanthanoid(III) complexes endowed with shift reagent capabilities are used to distinguish NMR resonances of species present in inner and outer cellular compartments and for measurement of pH and temperature. Among these are [Dy(ttha)]<sup>3-</sup> and [Tm(ttha)]<sup>3-</sup> [98AB]. NOTA complexes with lanthanoids have been proposed as aqueous shift reagents for biology [87GM, 85GS]. [Gd(cdta)]<sup>-\*</sup> is proposed for selective NMR line broadening for complex structure investigation in aqueous solutions [91PV].

\**trans*-2,2',2'',2'''-(cyclohexane-1,2-diyldinitri]l]tetraacetic acid, *trans*-1,2-cyclohexanediamine-*N,N,N',N''*-tetraacetic acid, CDTA, H<sub>4</sub>cdta.

Complexones have also been incorporated in complexes of  $^{99m}\text{Tc}$  and other radionuclides, to obtain scintigraphic imaging of human organs in diagnostic nuclear medicine [99VH, 98DP, 95AL, 88DT, 87AN]. The complex  $^{99m}\text{Tc}$ -DTPA has been approved for use as a kidney imaging agent [98DP].

Recently a new generation of compounds—bifunctional complexones—has been intensively studied for MRI and photometric or radioactive imaging and therapy [01LE, 00HF, 99CE, 99VH, 96SA, 95PT, 90SW, 86BG, 86ME, 84MW]. These bifunctional complexones assemble in the same molecule a chelating group (fragment of MIDA, EDTA, DTPA, TTHA, NOTA, DOTA, or TETA) and the chemically reactive functional group, which can be covalently attached to biological macromolecules. The structure illustrates a conjugate of TETA, linked through a  $\text{C}_4\text{S}$  spacer group to a protein lysine *N*-nitrogen [86ME]:



Complexones are widely studied and used for mobilization of heavy metals and radionuclides from contaminated soils [05BC, 99BS, 97PK, 95AH, 93HB]. Complexone properties can be advantageous in soil-washing decontamination technologies [97PK], but also disadvantageous by contributing to migration of low-level radionuclides from liquid-waste disposal pits [78MC]. Moreover, strong chelators such as DTPA can influence uptake of radionuclides by plants [81RW, 81WR, 81WW].

The broad and intensive applications of complexones require reliable stability constant data in order to allow equilibrium modeling and prediction of important technological, environmental, and pharmacokinetic equilibria [99BS, 96GM, 95GDa]. A direct relationship between stability constants and the toxicity of gadolinium and some other metals has been observed [00BC, 90CQa]. As complexones are resistant to biodegradation, chemical speciation calculations based on numerical equilibrium data are of extreme importance in environmental science, waste management, agriculture, magnetic resonance imaging, behavior of radiopharmaceuticals in blood plasma, and many other applications [05BC, 99BS, 95AH, 90CQa, 87SM, 84DMb].

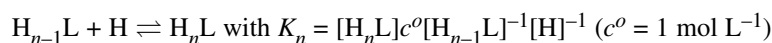
The data of interest are partly accumulated in a number of monographs [88DT, 71AN, 70PE], reviews [00BC, 87AN, 87SM], and compilations of stability constants [95IP, 91IP, 89MS, 87SM, 85IB]. Recently, three new computer databases have become commercially available [03IU, 97CS, 91MM]\*. The IUPAC Stability Constants Database [03IU] is the more comprehensive of these three and is taken here as the major source of data.

This review is based on data published in SC-Database [03IU]. The period 1965–1998 is covered exhaustively, but selected earlier and later publications are also included. References citing publications which include data not entered in [03IU] have the format “99AN”, etc. References taken from SC-Database use the database short reference format, e.g., “88THc”. In some cases, the SC-Database [03IU] gives one collective reference for several publications. For example, [72PRc] embraces data from six independent publications by the same authors. In this review, these publications are presented in a format “72PA, 72PB...72PZ” followed by the SC-Database short reference in the reference list. The names of journals are presented in original transcription followed by English version references (if any).

\*The latest versions available are: *Stability Constants Database and Mini-SCDatabase*. IUPAC and Academic Software, Version 5.3, 2003, Sourby Old Farm, Timble, Otley, Yorks, UK; <scdbase@acadsoft.co.uk>; NIST Standard Reference Database 46. *Critically Selected Stability Constants of Metal Complexes Database*, compiled by R. M. Smith, A. E. Martell, R. J. Motekaitis, Version 7.0 for Windows, 2003, U.S. National Institute of Standards and Technology Standard Reference Data Program, Gaithersburg, MD 20899; JESS: 'jess.murdoch.edu.au'.

## 2. PRESENTATION OF EQUILIBRIUM DATA AND ABBREVIATIONS USED

The stepwise protonation constants\* of ligands are presented as  $K_n$  for equilibrium



In tables, the equilibrium  $H_{n-1}L + H \rightleftharpoons H_nL$  is indicated in a brief form:  $H_{n-1}L + H$  and the corresponding constant as  $K(H_{n-1}L + H)$ . In all cases, L indicates species with all  $-\text{COOH}$  and ammonium groups deprotonated. M represents the cation and  $I$  symbolizes the ionic strength\*\*. Equilibria for metal-complexes are self-explanatory:  $M + L \rightleftharpoons ML$  is presented as  $M + L$  and  $K = [ML]c^o/[M][L]^{-1}$  as  $K_{ML}$  or  $K(M + L)$ ;  $M + H + L \rightleftharpoons MHL$  as  $M + H + L$  and  $K = [MHL](c^o)^2/[M][H][L]^{-1}$  as  $K(M + H + L)$  or as  $\beta_{MHL}$ ;  $M + HL \rightleftharpoons MHL$  as  $K(M + HL)$ , etc.

In potentiometric titrations with a glass electrode, the calibration technique governs the type of constant calculated. Concentration quotients (stability constants) are obtained when the electrode system is calibrated with solutions of known hydrogen ion concentration (e.g., a monoprotic strong acid) or by the conversion of pH values using the hydrogen ion activity coefficient. In the text, these are designated by "Conc.". Mixed constants [91SMa, 84PE] are obtained when standard buffer solutions of known hydrogen ion activity are used for electrode calibration (e.g., potassium hydrogen phthalate buffer with pH 4.008 at 25 °C). Such constants include both activity (hydrogen ions) and concentration (all other participants of the complexation equilibrium) terms. Following the reasons described elsewhere [91KSa, 91SMa, 84PE], priority is given to concentration constants.

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

gl	glass electrode (pH-metry)
EMF	metal electrode (e.m.f. measurement)
red	redox electrode (e.m.f. measurement)
ix	ion-exchange
sp	spectrophotometry
NMR	nuclear magnetic resonance
cal	calorimetry
dis	distribution
pol	polarography
kin	kinetic measurements
sol	solubility

## 3. GENERAL PHYSICOCHEMICAL PROPERTIES OF COMPLEXONES

Complexones ( $H_nL$ ) are generally poorly soluble in water (pH 2–3), while their alkali metal salts have a high solubility at pH > 4. At pH < 2, all complexones are capable of forming positively charged highly soluble species, such as  $H_3ida^+$ ,  $H_6dtpa^+$ ,  $H_7dtpa^{2+}$ ,  $H_7ttha^+$ , etc. The solubility of all complexones therefore attains a minimum between pH 1 and 4 [88DT, 83KDb, 67ANb]. This causes considerable accuracy problems in the measurement of protonation constants ( $\lg K_n$ ) of the neutral species  $H_nL$  and the ion  $H_{n+1}L^+$ .

The use of an incorrect or incomplete set of  $\lg K_n$  values may result in appreciable errors in calculated stability constants for highly stable complexes, for which measurements at low pH are required. The errors increase with the number of protonation constants that contribute significantly to the magnitude of  $[L]$  [77AN]. A very common error involves the neglect of positively charged ligand species

\*By common usage in solution chemistry, the term "protonation" refers to the natural isotopic mixture of hydrogen, not isotopically pure  $^1\text{H}$ . Strictly speaking, the reaction is "hydronation"; electric charges are omitted.

\*\*All the data (values) refer to amount concentrations ( $I_c$ ; mol dm $^{-3}$ ) unless otherwise stated. For reasons of brevity, mol L $^{-1}$  instead of mol dm $^{-3}$  is used.

that exist between pH 0 and 2; this is pertinent to spectrophotometric, electromigration, and other methodologies for the measurement of stability constants [73CC, 71BRa, 71EPb, 69DBa, 65BAC]. Some research groups recognized this problem, but did not have the required  $\lg K_n$  values to overcome it. For example, the formation of  $[\text{Bi}(\text{H}_4\text{ttha})]^+$ ,  $[\text{Bi}(\text{H}_3\text{ttha})]$ ,  $[\text{BiH}(\text{ttha})]^{2-}$ , and  $[\text{Bi}(\text{ttha})]^{3-}$  was established by spectrophotometry at  $\text{pH} < 2$ , but the authors failed to obtain the corresponding stability constants because “only six” of the required nine TTHA protonation constants were quantified [79NPa].

Discrepancies in  $\lg K(\text{L} + \text{H})$  values for all complexones, and  $\lg K(\text{HL} + \text{H})$  for DTPA, TTHA, DOTA, and NOTA are due to the binding of complexone anions to alkali metal ions of the background electrolytes used. The structure of  $[\text{Co}(\text{NH}_3)_6]_2[\text{Na}_2(\text{edta})_2\text{H}_2\text{O}] \cdot 6\text{H}_2\text{O}$  [88DT, 84PP] reveals that sodium coordinates to 2 nitrogen atoms and 4 oxygen atoms of EDTA. Thus, at appropriate pH alkali cations can efficiently compete with protons for nitrogen donor atoms of complexones. The most “neutral” (indifferent) cations for the system would seem to be tetramethylammonium or ammonium ions. Even though their ability to bind polyaminopolyacetates is not yet known, complexation of these cations is expected to be negligible in comparison to that of the alkali metal ions.

The interaction of alkali metal ions with macrocyclic complexones is rather strong. The protonation constant values for NOTA and DOTA were chosen, therefore, from those determined in  $(\text{CH}_3)_4\text{NCl}$  or  $(\text{CH}_3)_4\text{NNO}_3$  as supporting electrolytes. Since DOTA forms stable complexes with  $\text{Na}^+$ , and also with  $\text{K}^+$ , media containing these cations lead to anomalously low values for  $K(\text{L} + \text{H})$  and  $K(\text{HL} + \text{H})$ .

Another problem with DOTA measurements is the high value for the first protonation constant,  $K(\text{L} + \text{H})$ . In such cases,  $\lg K$  is difficult to determine by the usual potentiometric methods. NMR titration is the preferred technique, but current applications of this technique are unacceptable. Usually,  $\lg K(\text{L} + \text{H})$  values determined by NMR data are not accurate, owing to poor control of the ionic strength, to difficulties in preventing contact of the solution with the atmosphere, and the need to compare data obtained in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  media [91DSa]\*.

Complexones appear to interact with all known metal ions except possibly  $\text{Fr}^+$  [59ML]. For some metals, the highest reported stability constants have been observed with complexones. Strongly hydrolyzed cations, such as  $\text{Al}^{\text{III}}$ ,  $\text{In}^{\text{III}}$ ,  $\text{Tl}^{\text{III}}$ ,  $\text{Bi}^{\text{III}}$ ,  $\text{Zr}^{\text{IV}}$ ,  $\text{Th}^{\text{IV}}$ ,  $\text{Pd}^{\text{II}}$ , etc., are especially strongly complexed by complexones [03IU].  $K_{\text{ML}}$  values for many of these metals range between  $10^{30}$  and  $10^{40}$ . In these cases, direct potentiometric or spectrophotometric titrations cannot readily be used. Reaction with a competing ligand: 2,2',2''-triaminotriethylamine, (tren), 2,2'-{ethane-1,2-diylbis[(2-hydroxybenzyl)azanediyl]}diacetic acid, (*N,N'*-di-(2-hydroxybenzyl)-diaminoethane-*N,N'*-diacetic acid, HBED) [99DLa, 76AMa, 76HMd, 59CFc] or competing cation ( $\text{Hg}^{2+}$  [59CFc],  $\text{Ga}^{3+}$  [88THa],  $\text{Cu}^{2+}$  [72BCb]) is required. This in turn introduces additional systematic errors and problems. One such problem can arise owing to fairly slow kinetics of ligand–ligand displacement reactions, e.g., for  $\text{Fe}^{\text{III}}$  complexonates, equilibrium in most cases is established in a few days [90ADb].

$K_{\text{ML}}$  values have generally been determined in  $\text{KCl}$  or  $\text{KNO}_3$  media. The calculations have used ligand protonation constants obtained in solutions of potassium salts with no correction for  $\text{K}^+$  complexation. Such an approach can be accepted for IDA and MIDA, but not for DTPA, TTHA, and DOTA. Unfortunately, the stability constants of  $[\text{K}(\text{dtpa})]^{4-}$ ,  $[\text{Na}(\text{dtpa})]^{4-}$ , and  $[\text{K}(\text{ttha})]^{5-}$  are not yet published. It has been demonstrated that if published data need to be corrected for the formation of  $[\text{K}(\text{edta})]^{3-}$  in  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ , then the stability constant requires corrections by a factor of  $1 + [\text{K}^+]\text{K}_{\text{Kedta}}$  [77AN]. For  $\lg K_{\text{Medta}}$  the correction is +0.21. Taking into account the higher negative charge and denticity of DTPA and TTHA relative to EDTA, the corresponding  $\lg K_{\text{KL}}$  corrections are expected to be even higher.

The determination of stability constants for metal complexes of DOTA is highly dependent on the values used for  $K(\text{L} + \text{H})$  and  $K(\text{HL} + \text{H})$ . One of the reasons for the spread of values found in the literature for stability constants of complexes with this ligand is the variety of  $K(\text{L} + \text{H})$  values used by

\*IUPAC recommendations for NMR  $\lg K(\text{L} + \text{H})$  measurements are in preparation by K. Popov, H. Rönkkömäki, and L. H. J. Lajunen.

different authors. Those working with supporting  $\text{Na}^+$  electrolytes always report lower values of  $K_{\text{ML}}$ . The same situation occurs with those working with  $\text{K}^+$  electrolytes, but the lower stability constant for the  $\text{K}^+$ -DOTA complex can increase the comparative significance of other experimental errors.

The high potential denticity of complexones creates high (sometimes anomalously high) cation coordination numbers. For example, in  $[\text{Mg}(\text{H}_2\text{O})_6][\text{Mg}(\text{H}_2\text{O})\text{edta}] \cdot 2\text{H}_2\text{O}$  the magnesium ion chelated by EDTA has coordination number (CN) 7, while the other has CN 6 [84PP]. With the hexadentate ligand EDTA,  $\text{In}^{\text{III}}$  has CN 7 and forms five chelate rings in  $\text{Na}[\text{In}(\text{edta})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  [95IM], while with the octadentate DTPA it reveals CN 8 in  $\text{Na}_2[\text{In}(\text{dtpa})] \cdot 7\text{H}_2\text{O}$  and forms 7 chelate rings [89MR]. Thus, additional chelate rings are commonly formed relative to other complexes of the same cation with lower denticity ligands. Owing to high denticity, the most common species for DTPA, DOTA, TETA, and NOTA are ML and  $\text{MH}_n\text{L}$ , while complexes such as  $\text{M}(\text{OH})\text{L}$  are less common. ML complexes normally have mononuclear structures both in the solid state and in aqueous solution [88DT]. Thus, there are no special problems with association or polymerization of complexes.

TTHA is known to form  $\text{M}_2\text{L}/\text{ML}$  mixtures at 1:1 metal/ligand total concentration ratios. Ignorance of this fact has led to erroneous constants for  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  in [80KHb, 80MMd]. The same situation occurs for  $\text{Tl}^+$ ,  $\text{Tl}^{3+}$ , and many other cations. In contrast, MIDA and IDA are likely to form ML and  $\text{ML}_2$  species at 1:1 metal/ligand total concentration ratios, while  $\text{M}_2\text{L}$  is less common. ML complexes formed by MIDA and IDA have a higher tendency for hydrolysis, polymerization, and coagulation [88DT].

When all numerical values listed in [03IU] for complexones are compared, it appears that the relative internal consistency of data reported by one research group is much better than that observed between different groups. This causes serious problems for critical evaluation of lanthanoid lg  $K(\text{M} + \text{L})$  data. For this particular case, the difference in lg  $K(\text{M} + \text{L})$  between neighboring cations reported by one research group is much smaller than the difference between results obtained by different groups for the same element. Any attempt to present averaged values for a pair of neighboring lanthanoids leads to significant distortion of the trend in stability constants with increasing atomic number. In such cases, publications providing reliable stability constant trends for lanthanoids are identified in table footnotes, while the tables themselves present data for only one lanthanoid.

Protonation of ML (DTPA, TTHA, DOTA, TETA, NOTA) complexes does not necessarily lead to their decomposition [88DT]. For example, in  $\text{LaHedta} \cdot 7\text{H}_2\text{O}$  and  $\text{CoH}_2\text{edta} \cdot 3\text{H}_2\text{O}$  the carboxylate groups of EDTA are simultaneously protonated and coordinated [88DT]. In complexes formed by EDTA, DTPA, and TTHA the proton is normally localized on a carboxylate group, which either remains coordinated or leaves the metal ion coordination sphere. In the case of MIDA and IDA, protonation frequently occurs on the nitrogen atom. In this case, protonation leads to a complete decomposition of complex [88DT].

Kinetics of formation of ML is generally comparable with the rate of exchange of water molecules of aqueous-cations [78MA, 74MPa]. An exception arises with macrocyclic ligands (DOTA, TETA, and NOTA), and special precautions have to be taken to ensure an equilibrium state in stability constant measurements. For certain cations, such as  $\text{Ni}^{2+}$  and the lanthanoids, complex formation rates are very slow. In these cases, it is not possible to obtain reliable values by continuous titration methods, and the discontinuous or potentially less accurate batch process is required.

Most complexones are commercially available at high purity, with the exception of DOTA, TETA, and NOTA [82WB, 80DE, 77TT]. These macrocyclic compounds are prepared by several synthetic steps, and the purification of the final compound is difficult. Thus, the purity of the compounds used by some authors is not sufficient for accurate equilibrium constant determinations. For this reason, all the data obtained by [91CMA] and [91CMB] for DOTA were discarded. The separation of inorganic salts resulting from the synthesis of NOTA or DOTA can be made by ionic exchange chromatography, however, several authors do not perform this step. TETA is much less soluble in aqueous solutions and can be easily obtained without contamination by inorganic salts or other organic impurities.



At  $\text{pH} < 2$ , complexones are readily oxidized by cations such as  $\text{Ce}^{\text{IV}}$  or  $\text{Mn}^{\text{III}}$  even at room temperature [72YPa, 71BPh, 71MA, 71PMc, 71MAn, 70MMb]. Although this process is considerably slower at higher pH [88DT], all equilibrium data for these cations have been treated as doubtful.

Some special comments are needed with respect to TTHA. Because of the very large electrical charge of the ligand anion, maintenance of a constant ionic strength  $I$  (e.g.,  $I = 0.1 \text{ mol L}^{-1}$ ) is very difficult. A total TTHA concentration larger than  $1 \text{ millimol L}^{-1}$  should be avoided in strongly basic solutions. For instance, a  $1 \text{ millimol L}^{-1}$  solution of  $\text{K}_6\text{ttha}$  gives  $I = 0.021 \text{ mol L}^{-1}$ , i.e., more than 20 % of the ionic strength. This can be compensated in a titration only partially through the volume increase associated with strong base addition.

The calculation of equilibrium constants from pH measurements in solutions containing a metal ion and a complexone normally requires solutions free of complicated metal hydrolysis products. Some caution is therefore needed in the case of metal ions such as  $\text{Bi}^{3+}$ , which forms  $\text{Bi}_6(\text{OH})_{12}^{6+}$  below pH 1.5. Apparently, the authors of [69YMa] used data for the determination of the different constants of  $\text{Bi}^{3+}$  with TTHA without considering this fact.

#### 4. DATA EVALUATION CRITERIA

Each recommended value is normally based on a comparison of at least two independent high-quality publications. Data published on complexones have been evaluated by applying the following general criteria [01PRa, 97LP, 96YOa, 95SM, 91KSa, 91SMa, 75NB]:

- Clear definition of constants reported (i.e., unambiguous specification of complex stoichiometry MHL,  $\text{M}(\text{OH})\text{L}$ , etc., and of corresponding stability constants)\*.
- The extent to which essential reaction conditions (the purity of the ligand, temperature, ionic strength, 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) and specification whether concentration or mixed constants were calculated<sup>†</sup>.
- The maintenance of constant temperature and ionic strength during titrations<sup>††</sup>.
- Reliable treatment of the experimental data (e.g., careful consideration of all possible species formed: parent and mixed hydroxo-complexes of readily hydrolyzable metal ions, formation of dimers and polymers, cationic forms of a ligand, stability constants of competing ligand, etc.)<sup>‡</sup>.
- Correct selection of auxiliary data from the literature (e.g., selection of the concentration constants for ligand protonation required for the evaluation of spectrophotometric, magnetic relaxation or polarographic and pH measurements carried out on metal–ligand systems)<sup>‡‡</sup>.
- Details of the calculation method used<sup>#</sup>.

On the basis of these criteria, experimental data have been examined and initially grouped into two categories: “accepted” and “rejected”. Among those data that passed the preliminary acceptance

\*Most papers meet this requirement; the few exceptions [85MBb, 74TPa, 66LPa] were rejected.

\*\*This requirement was not met by [00BMa, 99SBd, 97YSa, 82VNa, 81DSa, 80KJa, 80OOb, 79MMf, 72KNb, 70KMe, 70MSd, 69HGa, 66KRa] and only for some of the studied ligands in [91CMA] and [91CMB], namely for DOTA.

†Such important information is missing in [85GAb, 80BTa, 75LBa, 72YPa, 71OBb, 56FRa] etc.

††This was not specified in [66STb].

‡References [90RNc, 88THa, 84HKa, 81DSa, 80MMd, 80KHb, 80KJa, 73CTa, 71GGa, 71GKb, 70HAa, 70KMe, 69YMa, 66EMd] have poor information in this field or errors (for which correction was sometimes possible).

‡‡Because of incorrect use of auxiliary data from the literature the following papers have been rejected or the obtained data have been corrected: [99DLA, 90CBc, 84HKa, 82OLa, 81DSa, 78RSa, 75NWa, 73CCc, 71BRa, 71EPb, 71LUa, 70HAa, 69KTC, 69YMa, 65BMf, 65KKa].

#Most papers published in 1945–1990 do not report on calculation methods used.

criteria, those that exhibited the best agreement were selected for further treatment. These were averaged, rounded and, depending on the standard deviations (s.d.), the mean values were regarded as **Recommended (R)**:  $s.d. \leq 0.05$  for H-complexes (e.g., H + L) and  $\leq 0.1$  for metal complexes (M + L, H + ML, or M + HL) or **Provisional (P)**:  $0.05 < s.d. \leq 0.2$  for H-complexes and  $0.1 < s.d. \leq 0.2$  for metal-complexes. The s.d. indicates therefore an agreement among the selected data and is included in Tables in parentheses. In those cases where the experimental uncertainty for each single value was much less than that derived from the mean value, then the latter is given. When the agreement of published data was better than experimental uncertainty, then the largest rounded s.d. from the original publication is listed. Although complexones have been studied intensively since 1945 and the total number of publications devoted to ligands of interest is about 480, data of sufficiently high quality have been found only in 99 papers. Therefore, for most metal–ligand combinations the group of “accepted” values did not allow comparison of stability constants measured by independent research group(s) under the same conditions. The amount of reliable data represented by a single group constituted 84 % (IDA), 95 % MIDA, 85 % (DTPA), 66 % (TTHA), 100 % (NOTA), 42 % (TETA), and 18 % (DOTA). Therefore, comparison between two or more independent research groups was impossible for the majority of values “accepted” in the preliminary selection.

In this situation, we nominated the data presented by a single research group as **Recommended 1 (R1)** if (a) we had no doubt as to the adequacy of applied experimental or calculation procedures and the research group has (b) either **R**-level agreement with Recommended values for other cations with similar properties (e.g., within lanthanoid or alkaline earth series), or revealed equally good agreement with independent researchers that measured the same constant for the same cation, but under slightly different experimental conditions (temperature, ionic strength). The former case can be illustrated by  $K^+$  and  $Ba^{2+}$  complexes of DOTA (Table 6), while the latter by  $K(HL + H)$  values for IDA, Table 1 (**R1** for 20 °C [76AMa] and **R** for 25 °C [86ANb, 71GKb]; both for 1 mol L<sup>-1</sup> NaClO<sub>4</sub>). In a few exceptional cases, the most reliable (and widely accepted) values are also nominated **R1**, for example, for  $Pd^{2+}$  complexes of DTPA, Table 3. The s.d. then reflects either the original value reported by the author or the one rounded by the reviewer, taking into account the level of agreement of this author’s other data with independent research.

In a similar way, category **P** was given to some results from single papers if the corresponding research group reveals **P**-level agreement with other researchers for at least one different cation. Provisional category was also given to those data having good agreement among several groups, but where the reviewers observed some deviations from the necessary rigor. In a few cases, values from a single publication that fit the general trend within **P**-level results has also been treated as Provisional, e.g.,  $Ra^{II}$  complexes with DTPA, Table 3.

It should be stressed that the formulation of uniform criteria for ligands of different denticity is not possible. For IDA and MIDA, the precision of stability constants should be as high as that found for Ni<sup>II</sup>-glycine [87BOa]; in contrast for DTPA, DOTA, TETA, and TTHA, it is significantly lower. For example, an evaluation of uncertainty in the constants for  $[(UO_2)_2dtpa]^-$  measured by direct potentiometric titration, gave a value of 0.36 lg units [82OLa]. In the case of competition reactions between complexones and another ligand (e.g., tren) for the metal ion, the uncertainty should be even larger owing to additional contribution of uncertainties associated with tren protonation and complexation.

In a few specific cases when evaluation identified some mistake in the determination of the constants, but these are nevertheless of semi-quantitative value, the criteria  $0.2 < s.d. \leq 0.3$  (lg  $K_{HL}$ ) and  $0.2 < s.d. \leq 1.0$  (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 footnotes. 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 including 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. References that are cited, but not included in the Tables could also be:

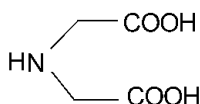
- communications with possibly correct data, but inadequate or poor description of experimental conditions, e.g., [80KJa, 80BTa];
- communications that reviewers could not access in the original version (in this case, an original reference is normally followed by *Chem. Abstr.*, IUPAC SC-Database, or some other secondary citation, indicating the place from which data are taken and the fact that they are not critically evaluated in the present Report);
- 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 requirements stated above, but owing to some hidden systematic errors reveal very large numerical discrepancies);
- publications that provide data for conditions that contrast with those for other data (e.g., high or low temperatures [86LDb, 81DMA, 67TMf], “unusual” ionic strengths [79ZLa, 76GAa], mixed solvents [95Lbb], ternary or mixed ligand complexes [98LVa, 97BH, 93BNb, 92Rkb, 91NBa, 90SSc, 90UBc, 87FZa, 79BCa, 79KNa, 78KNc, 76PAa, 76PTb], effective or conditional stability constants [75BUb, 75HTa], etc.);
- publications that present only enthalpy values.

The ligands are considered in the order of increasing complexity. The stability constants of metal complexes are surveyed in the following groups of the periodic table: hydrogen ion, groups 1, 2, 13, 14, 15, 3*d*-group; 4*d*-5*d*-groups, group 3, and a group of 4*f*-5*f* 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 that contributed to the mean value listed in the table. When the average value is derived from data obtained in different media, then symbols like Na/KCl or KCl/NO<sub>3</sub> are used.

The reviewers did not recalculate stability constants to a uniform ionic strength. With the exception of a few values that were recalculated for TTHA complexes using more reliable ligand protonation constants, the data listed represent an average of those reported in the accepted publications. Critically evaluated data are presented in Tables 1–7.

## 5. 2,2'-AZANEDIYLDIACETIC ACID (IMINODIACETIC ACID), IDA, H<sub>2</sub>ida



*Cations studied*<sup>a–f</sup>: H<sup>+</sup>: 00Bma, 99SBb, 99SEb, 95MAa, 94Tsa, 92ANa, 92CGa, 92GLa, 92RAc, 89MIa, 88THa, 87FZa, 87MDa, 86ANb, 85HAc, 83DBb, 83Fsa, 83SVa, 82NBa, 82VNa, 81DSa, 81MOa, 80OOb, 79ZLa, 78JSb, 78MGa, 78RSa, 77PTb, 76AMa, 76GMb, 75MRb, 73CBc, 73CTa, 73SKb, 73STc, 72NAa, 71BB, 71GGa, 71GKb, 71LNB, 71TSh, 70KMe, 70NPc, 69PMd, 68Ksa, 67MY, 67SKg, 67TMg, 66KRa, 66MAb, 64ANa, 64RMc, 62THa, 52Cma, 45SKa

<b>Be<sup>2+</sup></b> b :	87MDa, 81DSa	90UBc, 87NDA,	<b>Ce<sup>3+</sup></b> :	88VSc, 79TKb, 76TBb,
<b>Mg<sup>2+</sup></b> e :	95LBb, 69ASb, 64ANa, 45SKa	85KVa, 85SNa,		71GKb, 62THa
<b>Ca<sup>2+</sup></b> e :	75MRb, 69ASb, 68KSa, 64ANa, 57TBb, 45SKa	85SRc, 84HKa, 83FSa, 83SVa, 82VRa, 81FMb, 80NWA, 79BCa, 78WIA, 76KIA,	<b>Pr<sup>3+</sup></b> :	88VSc, 84KTb, 80KTb, 72GGa, 71GKb, 62THa
<b>Sr<sup>2+</sup></b> :	69ASb, 64ANa	75NWA, 73YBa, 71TSh, 71TSj, 70STf, 69LAA, 69STb, 67TMg, 64ANa, 57SYb, 57TBb, 52CMA	<b>Nd<sup>3+</sup></b> :	88VSc, 84KTb, 80KTb, 74PLa, 74TDa, 73TEb, 71GKb, 70KMe, 69PMd, 68KRC, 67TKa, 66KTA, 62THa
<b>Ba<sup>2+</sup></b> :	64ANa, 45SKa		<b>Sm<sup>3+</sup></b> :	88VSc, 71GKb, 62THa
<b>Al<sup>3+</sup></b> b :	97Ysa, 81DSa, 71LNb		<b>Eu<sup>2+</sup></b> :	73CTa
<b>Ga<sup>3+</sup></b> :	97Ysa, 85Saa, 76HMD	<b>Zn<sup>2+</sup></b> :	<b>Eu<sup>3+</sup></b> :	88VSc, 76TBb, 73CTa, 72GGa, 71GGA, 71GKb, 71TKf, 66MAB, 62THa
<b>In<sup>3+</sup></b> :	97Ysa, 85MMA, 85Saa, 84PGA, 66MAB	92GLa, 92NAa, 92RAC, 85SNa, 83VRA, 81FMb, 78KCa, 73HAb, 71TSh, 71TSj, 70FDa, 70STf, 64ANa, 57SYb, 52CMA	<b>Gd<sup>3+</sup></b> :	88VSc, 84KTb, 80KTb, 71GKb, 62THa
<b>Tl<sup>+</sup></b> :	70FUB		<b>Tb<sup>3+</sup></b> :	88VSc, 76TBb, 71GKb, 62THa
<b>Sn<sup>IV</sup></b> :	92CGa		<b>Dy<sup>3+</sup></b> :	88VSc, 84KTb, 80KTb, 71GKa, 62THa
<b>Pb<sup>2+</sup></b> :	83FSa, 81MOa, 80NWA, 76KIA, 76NCA, 72NAa, 71KTD, 64ANa	<b>Cd<sup>2+</sup></b> :	<b>Ho<sup>3+</sup></b> :	74PLa, 72GGa, 71GKa, 62THa
<b>Bi<sup>3+</sup></b> :	76KIA	95LBb, 92GLa, 84MRA, 83SVA, 83YWA, 81GKa, 78KCa, 71TSh, 71TSj, 70STf, 64ANa, 57SYb, 52CMA	<b>Er<sup>3+</sup></b> :	74PLa, 71GKb, 71TKf, 71TSh, 62THa
<b>V<sup>V</sup></b> :	79ZLa		<b>Tm<sup>3+</sup></b> :	71GKa, 62THa
<b>VO<sup>2+</sup></b> :	99SBb, 84FVa, 83FSa, 78JSb, 73STc, 66KFc	<b>Hg<sup>2+</sup></b> :	<b>Yb<sup>3+</sup></b> :	71GKb, 69PMd, 62THa
<b>Cr<sup>2+</sup></b> :	83MDb	75LBA, 67SKg	<b>Lu<sup>3+</sup></b> :	72GGa, 71GKb, 62THa
<b>Cr<sup>3+</sup></b> :	82VNa, 81DSa, 70MSd	<b>Hg<sub>2</sub><sup>2+</sup></b> :	<b>UO<sub>2</sub><sup>2+</sup></b> :	84BLb, 82NBa, 80BTa, 73CBc, 67Lca, 64RMc
<b>Fe<sup>2+</sup></b> :	00BMA, 72Nac, 64ANa	67SKg	<b>NpO<sub>2</sub><sup>+</sup></b> f :	94Tsa, 90Rnc, 83ITa, 73CBc, 70Ewa, 70KC
<b>Fe<sup>3+</sup></b> :	00BMA, 99SEb, 97Ysa, 86ANb, 72NAb	<b>Ag<sup>I</sup></b> :	<b>Am<sup>3+</sup></b> :	89Rsa, 71BB, 69DBa
<b>Co<sup>2+</sup></b> :	87Fza, 84Vra, 83DBb, 80OOb, 64ANa, 52CMA	<b>Zr<sup>4+</sup></b> :	<b>PuO<sub>2</sub><sup>+</sup></b> :	73CBc, 70Ewa
<b>Co<sup>3+</sup></b> :	76BCb, 69BHb	64Pvc	<b>Th<sup>4+</sup></b> :	85Saa, 83BCa, 82NBa, 77PTb, 74Kpd, 73SKb
<b>Ni<sup>2+</sup></b> :	92GLa, 90UBc, 84VKb, 83FSa, 81ACA, 71TSh, 71TSj, 70CMA, 70Npc, 69FDa, 64ANa, 57TBb, 52CMA	<b>Hf<sup>4+</sup></b> :		
<b>Cu<sup>2+</sup></b> :	95LBb, 92GLa, 92NAa, 92Rac, 92RKb,	78Rsa		
		<b>Mo<sup>VI</sup></b> :		
		79ZLa, 66KRra		
		<b>W<sup>VI</sup></b> :		
		79ZLa, 66KRra		
		<b>Pd<sup>2+</sup></b> :		
		76AMA, 75CGc, 75Vca		
		<b>Ru<sup>3+</sup></b> :		
		88THa		
		<b>Sc<sup>3+</sup></b> :		
		97Ysa, 85Saa, 80SKc, 74Kpd, 72GGa		
		<b>Y<sup>3+</sup></b> :		
		97Ysa, 71GKb, 62THa		
		<b>La<sup>3+</sup></b> :		
		97Ysa, 88VSc, 84KTb, 80KTb, 76TBb, 74Kpd, 71GKb, 64ANa, 62THa		

*Experimental conditions of papers selected for critical evaluation:*

$I = 0.1 \text{ mol L}^{-1} \text{ KNO}_3$ , 20 °C, Conc., gl: 64ANa

$I = 0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ , 25 °C, Conc., gl: 81DSa

$I = 0.1 \text{ mol L}^{-1} \text{ KCl}$ , 25 °C, Conc., gl: 88THa

$I = 0.1 \text{ mol L}^{-1} \text{ KNO}_3$ , 25 °C, Conc., gl: 92CGa, 84FVa, 83FSa, 82NBa, 78JSb, 62THa; EMF: 83SVa

$I = 0.1 \text{ mol L}^{-1} \text{ Me}_4\text{NBr}$ , 25 °C, Conc., sp: 85HAc

$I = 0.1 \text{ mol L}^{-1} \text{ KCl}$ , 30 °C, Conc., gl: 52CMA

$I = 0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ , 35 °C, Conc., gl: 81DSa

$I = 0.2 \text{ mol L}^{-1} \text{ KCl}$ , 25 °C, Conc., gl: 99SBb

$I = 0.5 \text{ mol L}^{-1} \text{ NaClO}_4$ , 25 °C, Conc., gl: 92GLa, 87MDa, 73CTa, 72NAa, 72NAc, 71LNb

$I = 0.5 \text{ mol L}^{-1} \text{ KNO}_3$ , 25 °C, Conc., gl.: 99SEb

$I = 1.0 \text{ mol L}^{-1} \text{ NaClO}_4$ , 20 °C, Conc., gl: 76AMa, 73CBc

$I = 1.0 \text{ mol L}^{-1} \text{ NaNO}_3$ , 25 °C, Conc., gl: 95MAa

$I = 1.0 \text{ mol L}^{-1} \text{ NaClO}_4$ , 25 °C, Conc., gl: 86ANb, 71GGa, 71GKb

$I = 1.0 \text{ mol L}^{-1} \text{ KNO}_3$ , 25 °C, Conc., gl: 92ANa, 81MOa, 64RMc

$I = 1.0 \text{ mol L}^{-1} \text{ KCl}$ , 25 °C, Conc., gl: 78MGa, 76GMb

**Table 1** Recommended and provisional data for IDA.

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
$\text{H}^+$	H + L	0.1; $\text{Me}_4\text{NBr}$	25	9.45 (0.01)	P	85HAc
		0.1; $\text{KNO}_3$	20	9.45 (0.02)	P	64ANa
		0.1; $\text{KNO}_3/\text{Cl}$	25	9.32 (0.02)	R	92CGa, 88THa, 83FSa, 83SVa, 82NBa, 78JSb, 62THa
		0.2; KCl	25	9.29 (0.03)	P	99SBb
		0.5; $\text{KNO}_3$	25	9.25 (0.06)	P	99SEb
		1.0; $\text{KNO}_3/\text{Cl}$	25	9.27 (0.03)	R	92ANa, 81MOa, 78MGa
		0.1; $\text{NaClO}_4$	35	9.25 (0.06)	P	81DSa
		0.5; $\text{NaClO}_4$	25	9.22 (0.05)	R	87MDa, 72NAa, 71LNa
		1.0; $\text{NaClO}_4$	20	9.33 (0.08)	P	76AMa, 73CBc
	1.0; $\text{NaClO}_4$	25	9.29 (0.05)	R1	86ANb	
	HL + H	0.1; $\text{KNO}_3/\text{Cl}$	25	2.60 (0.03)	R	92CGa, 88THa, 83FSa, 62THa
		0.2; KCl	25	2.54 (0.04)	P	99SBb
		0.5; $\text{KNO}_3$	25	2.53 (0.06)	P	99SEb
		1.0; $\text{KNO}_3/\text{Cl}$	25	2.60 (0.03)	R	81MOa, 78MGa
		0.1; $\text{NaClO}_4$	25	2.70 (0.07)	P	81DSa
		0.1; $\text{NaClO}_4$	35	2.66 (0.03)	P	81DSa
		0.5; $\text{NaClO}_4$	25	2.58 (0.02)	R	92CGa, 87MDa, 73CTa, 72NAa, 71LNa
		1.0; $\text{NaClO}_4$	20	2.64 (0.03)	R1	76AMa
		1.0; $\text{NaNO}_3$	25	2.65 (0.04)	R1	95MAa
	1.0; $\text{NaClO}_4$	25	2.58 (0.03)	R	71GKb, 86ANb	
	$\text{H}_2\text{L} + \text{H}$	1.0; $\text{KNO}_3/\text{Cl}$	25	1.82 (0.06)	P	81MOa, 76GMb
0.5; $\text{NaClO}_4$		20	1.8 (0.1)	P	76AMa	
0.5; $\text{NaClO}_4$		25	1.79 (0.03)	P	87MDa	
1.0; $\text{NaClO}_4$		25	1.87 (0.02)	R	86ANb, 71GGa	
$\text{Mg}^{2+ \text{ e}}$	M + L	0.1; $\text{KNO}_3$	20	2.94 (0.05)	P	64ANa
$\text{Ca}^{2+ \text{ e}}$	M + L	0.1; $\text{KNO}_3$	20	2.59 (0.05)	P	64ANa
$\text{Sr}^{2+}$	M + L	0.1; $\text{KNO}_3$	20	2.23 (0.05)	P	64ANa
$\text{Ba}^{2+}$	M + L	0.1; $\text{KNO}_3$	20	1.67 (0.05)	P	64ANa
$\text{Sn}^{\text{IV}}$	$(\text{SnMe}_2)^{2+} + \text{L}$	0.1; $\text{KNO}_3$	25	9.4 (0.1)	P	92CGa

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**Table 1** (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References	
Pb <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	20	7.45 (0.03)	P	64ANa	
		0.1; KNO <sub>3</sub>	25	7.41 (0.01)	P	83FSa	
		0.5; NaClO <sub>4</sub>	25	7.3 (0.1)	P	72NAa	
	M + H + L	0.5; NaClO <sub>4</sub>	25	10.4 (0.1)	P	72NAa	
	M + 2H + L	0.5; NaClO <sub>4</sub>	25	12.7 (0.1)	P	72NAa	
VO <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	25	9.00 (0.01)	P	84FVa, 83FSa	
		0.2; KCl	25	8.84 (0.02)	P	99SBb	
	M + 2L	0.2; KCl	25	15.32 (0.06)	P	99SBb	
Fe <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	20	5.8 (0.1)	P	64ANa	
		0.5; NaClO <sub>4</sub>	25	5.1 (0.1)	P	72NAc	
	M + 2L	0.1; KNO <sub>3</sub>	20	10.0 (0.1)	P	64ANa	
		0.5; NaClO <sub>4</sub>	25	9.8 (0.2)	P	72NAc	
Fe <sup>3+</sup>	M + L	0.5; KNO <sub>3</sub>	25	10.90 (0.02)	P	99SEb	
		1.0; NaClO <sub>4</sub>	25	11.1 (0.2)	P	86ANb	
	M + 2L	0.5; KNO <sub>3</sub>	25	19.33 (0.03)	P	99SEb	
Co <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	20	6.97 (0.05)	P	64ANa	
		0.1; KCl	30	6.95 (0.02)	P	52CMa	
	M + 2L	0.1; KNO <sub>3</sub>	20	12.3 (0.2)	P	64ANa	
		0.1; KCl	30	12.3 (0.1)	P	52CMa	
Ni <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	20	8.19 (0.03)	P	64ANa	
		0.1; KNO <sub>3</sub>	25	8.13 (0.03)	P	83FSa	
	M + 2L	0.1; KNO <sub>3</sub>	20	14.3 (0.1)	P	64ANa	
	Cu <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	20	10.6 (0.2)	P	64ANa
			0.1; KNO <sub>3</sub>	25	10.6 (0.1)	P	83FSa
0.1; KCl			30	10.55 (0.08)	P	52CMa	
M + 2L	0.1; KNO <sub>3</sub>	25	16.3 (0.1)	P	83SVa		
	0.1; KCl	30	16.20 (0.05)	P	52CMa		
Zn <sup>2+</sup>	M + L	0.1; KCl	30	7.03 (0.02)	P	52CMa	
		0.5; NaClO <sub>4</sub>	25	7.0 (0.1)	P	92GLa	
	M + 2L	0.5; NaClO <sub>4</sub>	25	12.4 (0.1)	P	92GLa	
Cd <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	20	5.7 (0.2)	P	64ANa	
		0.5; NaClO <sub>4</sub>	25	5.55 (0.02)	P	92GLa	
		0.1; KNO <sub>3</sub>	25	5.48 (0.05)	P	83SVa	
		0.1; KCl	30	5.4 (0.2)	P	52CMa	
	M + 2L	0.5; NaClO <sub>4</sub>	25	9.99 (0.02)	P	92GLa	
Ag <sup>+</sup>	M + L	1.0; KNO <sub>3</sub>	25	3.27 (0.02)	P	92ANa	
	M + 2L	1.0; KNO <sub>3</sub>	25	5.90 (0.05)	P	92ANa	
Pd <sup>2+</sup>	M + L	1.0; NaClO <sub>4</sub>	20	17.5 (0.1)	R1	76AMa	
	ML + L	1.0; NaClO <sub>4</sub>	20	9.3 (0.1)	R1	76AMa	
Y <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.8 (0.1)	P	62THa	
	M + 2L	0.1; KNO <sub>3</sub>	25	12.0 (0.1)	P	62THa	

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Table 1 (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
La <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	5.9 (0.1)	P	62THa
	M + 2L	0.1; KNO <sub>3</sub>	20	9.7 (0.2)	P	64ANa
		0.1; KNO <sub>3</sub>	25	10.0 (0.2)	P	62THa
Ce <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.2 (0.1)	P	62THa
	M + 2L	0.1; KNO <sub>3</sub>	25	10.7 (0.1)	P	62THa
Pr <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.4 (0.1)	P	62THa
	M + 2L	0.1; KNO <sub>3</sub>	25	11.2 (0.1)	P	62THa
Nd <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.54 (0.04)	P	62THa
Sm <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.6 (0.1)	P	62THa
Eu <sup>2+</sup>	M + L	0.5; NaClO <sub>4</sub>	25	4.9 (0.1)	P	73CTa
	M + 2L	0.5; NaClO <sub>4</sub>	25	7.5 (0.1)	P	73CTa
Eu <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.7 (0.1)	P	62THa
		0.5; NaClO <sub>4</sub>	25	6.62 (0.06)	P	73CTa
		1.0; NaClO <sub>4</sub>	25	6.48 (0.08)	R	71GGa, 71GKb
	M + 2L	0.1; KNO <sub>3</sub>	25	12.1 (0.1)	P	62THa
		1.0; NaClO <sub>4</sub>	25	11.65 (0.05)	R	71GGa, 71GKb
	M + 3L	0.5; NaClO <sub>4</sub>	25	15.5 (0.2)	P	73CT
	1.0; NaClO <sub>4</sub>	25	15.70 (0.03)	R	71GGa, 71GKb	
Gd <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.68 (0.05)	P	62THa
	M + 2L	0.1; KNO <sub>3</sub>	25	12.1 (0.1)	P	62THa
Tb <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.78 (0.15)	P	62THa
Dy <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	6.9 (0.1)	P	62THa
Ho <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	7.0 (0.2)	P	62THa
Er <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	7.1 (0.1)	P	62THa
	M + 2L	0.1; KNO <sub>3</sub>	25	12.7 (0.1)	P	62THa
Tm <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	7.2 (0.1)	P	62THa
	M + 2L	0.1; KNO <sub>3</sub>	25	12.9 (0.1)	P	62THa
Yb <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	7.4 (0.1)	P	62THa
	M + 2L	0.1; KNO <sub>3</sub>	25	13.3 (0.1)	P	62THa
Lu <sup>3+</sup>	M + L	0.1; KNO <sub>3</sub>	25	7.6 (0.1)	P	62THa
	M + 2L	0.1; KNO <sub>3</sub>	25	13.7 (0.1)	P	62THa
UO <sub>2</sub> <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	25	8.73 (0.04)	P	82NBa
		1.0; NaClO <sub>4</sub>	20	8.7 (0.1)	P	73CBc
		1.0; KNO <sub>3</sub>	25	8.73 (0.04)	P	64RMc
	M + 2L	0.1; KNO <sub>3</sub>	25	17.28 (0.05)	P	82NBa

<sup>a</sup>Owing to the fact that IDA has been studied since 1945 [45SKa], there are many results, especially for its protonation, at temperatures of 20 or 25 °C. At the same time, for physiological conditions ( $I = 0.15 \text{ mol L}^{-1} \text{ NaClO}_4$ , 37 °C) only a single paper [92RAc] (Conc., gl) seems to present reliable data, although even these do not meet all the requirements for recommendation. The data presented by [92RAc] are also in disagreement with two other papers for similar conditions ( $I = 0.10 \text{ mol L}^{-1} \text{ KNO}_3$ , 35 °C) [78RSa, 77PTb].

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**Table 1** (Continued).

<sup>b</sup>The values for the formation constants of the complexes with some ions demonstrate a very large disparity. It was not possible to recommend values for  $\text{Al}^{3+}$ : the two publications on Al-IDA complexes [81DSa, 71LNb] reveal a large disagreement, likely because of different metal ion hydrolysis models and values being assumed. The results for  $\text{Cr}^{3+}$  show a large disparity [82VNa, 81DSa, 70MSd] associated with an inappropriate account of slow formation of the complexed species of this ion.

The  $\text{Be}^{2+}$  species are represented in two publications. One paper [81DSa] does not take account of the hydrolyzed species of the metal ion and of the complexes. The other paper has better-quality data [87MDa], but further independent research is needed for reliable evaluation.

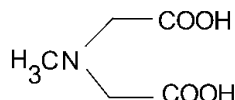
<sup>c</sup>There are also many cases where the formation constants of the complexes are in good agreement, but the data were not recommended because the protonation constant values for the ligand were assessed to be incorrect when compared with the **Recommended** values (e.g., [84HKa] and [78RSa]).

<sup>d</sup>For  $\text{Ln}^{3+}$ , the generally reliable reference [62THa] does not take into account the possible formation of  $\text{LnL}_3$  complexes in 1:2 metal/ligand total molar ratio mixture [70KMe, 71GGa, 71GKb, 73CTa].

<sup>e</sup>The trend found in [64ANa] for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  IDA complexes ( $\lg K_{\text{MgL}} > \lg K_{\text{CaL}}$ ) is the inverse of that for MIDA [68NPb, 55SAa], Table 2. Thus, the corresponding data need further support by an independent study of both IDA and MIDA complexes with  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

<sup>f</sup>Values of  $\lg K(\text{M} + \text{L})$  reported for  $\text{NpO}_2^+$ -IDA complexes range from 5.64 to 8.72 [94TSa, 90RNc, 83ITa, 73CBc, 70EWa]. The value  $\lg K(\text{M} + \text{L}) = 6.4$  (0.3) [94TSa], can be treated as reliable (1.0 mol  $\text{L}^{-1}$   $\text{NaClO}_4$ , 25 °C, Conc., dis) although outside of the "Provisional" range.

## 6. 2,2'-(METHYLZANEDIYL)DIACETIC ACID, ((METHYLIMINO)DIACETIC ACID), MIDA, $\text{H}_2\text{mida}$



*Cations studied* <sup>a-e</sup>:  $\text{H}^+$  <sup>b</sup>: 99SEb, 96ANb, 92GLa, 87MDa, 86MDa, 83FSa, 79MMd, 77MGb, 77NAa, 77Tia, 76YNa, 75MRb, 70FSa, 68NPb, 66KRa, 66KUa, 65ANa, 56OMa, 55SAa, 45SKa

<b>Be<sup>2+</sup></b> : 87MDa	<b>Fe<sup>2+</sup></b> : 86MDa, 77Tia, 55SAa	<b>Y<sup>3+</sup></b> : 80MGc
<b>Mg<sup>2+</sup></b> <sup>e</sup> : 77Tia, 69VPa, 68NPb, 65ANa, 56MAa, 55SAa, 45SKa	<b>Fe<sup>3+</sup></b> : 99SEb	<b>La<sup>3+</sup></b> : 80MGc, 72KNb
<b>Ca<sup>2+</sup></b> <sup>e</sup> : 75MRb, 69VPa, 68NPb, 65ANa, 55SAa, 45SKa	<b>Co<sup>2+</sup></b> : 77Tia, 73IVa, 72IVa, 65ANa, 55SAa	<b>Pr<sup>3+</sup></b> : 80MGc
<b>Sr<sup>2+</sup></b> : 68NPb, 65ANa, 56MAa, 55SAa	<b>Ni<sup>2+</sup></b> : 92GLa, 83FSa, 77Tia, 73IVa, 72IVa, 70CMA, 69VPa, 65ANa, 55SAa	<b>Nd<sup>3+</sup></b> <sup>d</sup> : 80MGc, 79MMf
<b>Ba<sup>2+</sup></b> : 68NPb, 65ANa, 55SAa, 45SKa	<b>Cu<sup>2+</sup></b> : 92GLa, 83FSa, 77Tia, 73IVa, 72IVa, 69VPa, 65ANa, 55SAa	<b>Sm<sup>3+</sup></b> : 80MGc, 77Tia
<b>Al<sup>3+</sup></b> : 84NAa	<b>Zn<sup>2+</sup></b> : 92GLa, 77MGb, 73HAb, 65ANa, 45SKa	<b>Eu<sup>3+</sup></b> : 80MGc
<b>Pb<sup>2+</sup></b> : 85NAa, 83FSa, 69VPa, 65ANa, 45SKa	<b>Cd<sup>2+</sup></b> : 92GLa, 73IVa, 72IVa, 65ANa, 55SAa	<b>Gd<sup>3+</sup></b> : 80MGc
<b>Sn<sup>IV</sup></b> : 97TNa, 96ANb		<b>Tb<sup>3+</sup></b> : 80MGc
<b>V<sup>V</sup></b> : 76YNa		<b>Dy<sup>3+</sup></b> : 80MGc
<b>VO<sup>2+</sup></b> : 83FSa, 77NAa	<b>Hg<sup>2+</sup></b> : 55SAa	<b>Ho<sup>3+</sup></b> : 80MGc
<b>Cr<sup>2+</sup></b> : 86MNa, 82CGa, 76BDa	<b>Mo<sup>VI</sup></b> : 66KRa, 66KUa	<b>Er<sup>3+</sup></b> : 80MGc
<b>Mn<sup>2+</sup></b> : 69VPa, 65ANa, 56MAa, 55SAa	<b>W<sup>VI</sup></b> : 66KRa	<b>Tm<sup>3+</sup></b> : 80MGc
	<b>Pd<sup>2+</sup></b> : 87KUa	<b>Yb<sup>3+</sup></b> : 80MGc
		<b>Lu<sup>3+</sup></b> : 80MGc, 72KNb
		<b>UO<sub>2</sub><sup>2+</sup></b> : 70FSa
		<b>NpO<sub>2</sub><sup>2+</sup></b> : 90RNc, 70EWa



*Experimental conditions of papers selected for critical evaluation:* $I = 0.1 \text{ mol L}^{-1}$  KCl, 20 °C, Conc., gl: 55SAa $I = 0.1 \text{ mol L}^{-1}$  NaClO<sub>4</sub>, 25 °C, Conc., gl: 68NPb $I = 0.1 \text{ mol L}^{-1}$  KNO<sub>3</sub>, 25 °C, Conc., gl: 83FSa, 70FSa $I = 0.1 \text{ mol L}^{-1}$  KCl, 25 °C, Conc., gl: 86MDa, 68NPb $I = 0.5 \text{ mol L}^{-1}$  NaClO<sub>4</sub>, 25 °C, Conc., gl: 92GLa, 87MDa, 84NAa, 77NAa $I = 0.5 \text{ mol L}^{-1}$  KNO<sub>3</sub>, 25 °C, Conc., gl.: 99SEb $I = 1.0 \text{ mol L}^{-1}$  NaClO<sub>4</sub>, 25 °C, Conc., gl: 76YNa**Table 2** Recommended and provisional data for MIDA.

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
$\text{H}^+$ <sup>b</sup>	H + L	0.1; KCl	20	9.65 (0.07)	P	55SAa
		0.1; KCl/NO <sub>3</sub>	25	9.59 (0.02)	R	86MDa, 68NPb, 83FSa
		0.5; NaClO <sub>4</sub>	25	9.43 (0.03)	R	92GLa, 77NAa
		0.5; KNO <sub>3</sub>	25	9.46 (0.03)	R1	99SEb
		1.0; NaClO <sub>4</sub>	25	9.48 (0.06)	P	76YNa
	HL + H	0.1; KCl	20	2.12 (0.09)	P	55SAa
		0.5; NaClO <sub>4</sub>	25	2.28 (0.02)	R	92GLa, 87MDa
		0.5; KNO <sub>3</sub>	25	2.32 (0.03)	R1	99SEb
		1.0; NaClO <sub>4</sub>	25	2.4 (0.1)	P	76YNa
	H <sub>2</sub> L + H	0.5; KNO <sub>3</sub>	25	1.4 (0.1)	P	99SEb
		1.0; NaClO <sub>4</sub>	25	1.6 (0.1)	P	76YNa
	$\text{Mg}^{2+}$ <sup>e</sup>	M + L	0.1; KCl	20	3.4 (0.1)	P
0.1; NaClO <sub>4</sub>			25	3.5 (0.1)	P	68NPb
M + 2L		0.1; NaClO <sub>4</sub>	25	5.83 (0.05)	P	68NPb
$\text{Ca}^{2+}$ <sup>e</sup>	M + L	0.1; KCl	20	3.8 (0.1)	P	55SAa
		0.1; NaClO <sub>4</sub>	25	3.9 (0.1)	P	68NPb
	M + 2L	0.1; NaClO <sub>4</sub>	25	6.6 (0.1)	P	68NPb
$\text{Sr}^{2+}$	M + L	0.1; KCl	20	2.9 (0.1)	P	55SAa
		0.1; NaClO <sub>4</sub>	25	3.0 (0.1)	P	68NPb
	M + 2L	0.1; NaClO <sub>4</sub>	25	4.8 (0.1)	P	68NPb
$\text{Ba}^{2+}$	M + L	0.1; KCl	20	2.6 (0.1)	P	55SAa
		0.1; NaClO <sub>4</sub>	25	2.6 (0.1)	P	68NPb
	M + 2L	0.1; NaClO <sub>4</sub>	25	4.9 (0.1)	P	68NPb
$\text{Al}^{3+}$	M + L	0.5; NaClO <sub>4</sub>	25	7.6 (0.1)	P	84NAa
$\text{Pb}^{2+}$	M + L	0.1; KNO <sub>3</sub>	25	7.94 (0.05)	P	83FSa
		0.1; KCl	20	8.0 (0.1)	P	55SAa
	M + 2L	0.1; KCl	20	12.1 (0.1)	P	55SAa
$\text{VO}_2^+$	M + L	1.0; NaClO <sub>4</sub>	25	10.2 (0.1)	P	76YNa
$\text{VO}^{2+}$	M + L	0.1; KNO <sub>3</sub>	25	9.56 (0.06)	P	83FSa
		0.5; NaClO <sub>4</sub>	25	9.44 (0.06)	P	77NAa
$\text{Mn}^{2+}$	M + L	0.1; KCl	20	5.4 (0.1)	P	55SAa
	M + 2L	0.1; KCl	20	9.6 (0.1)	P	55SAa

*(continues on next page)*

**Table 2** (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
$\text{Fe}^{2+}$	M + L	0.1; KCl	20	6.7 (0.1)	P	55SAa
		0.1; KCl	25	6.71 (0.04)	P	86MDa
	M + 2L	0.1; KCl	20	12.0 (0.1)	P	55SAa
		0.1; KCl	25	11.8 (0.1)	P	86MDa
$\text{Fe}^{3+}$	M + L	0.5; $\text{KNO}_3$	25	10.99 (0.03)	P	99SEb
	M + 2L	0.5; $\text{KNO}_3$	25	20.72 (0.03)	P	99SEb
$\text{Co}^{2+}$	M + L	0.1; KCl	20	7.6 (0.1)	P	55SAa
	M + 2L	0.1; KCl	20	13.9 (0.1)	P	55SAa
$\text{Ni}^{2+}$	M + L	0.1; KCl	20	8.7 (0.1)	P	55SAa
		0.1; $\text{KNO}_3$	25	8.7 (0.1)	P	83FSa
		0.5; $\text{NaClO}_4$	25	8.5 (0.1)	P	92GLa
	M + 2L	0.1; KCl	20	15.9 (0.1)	P	55SAa
$\text{Cu}^{2+}$	M + L	0.1; KCl	20	11.1 (0.1)	R1	55SAa
		0.1; $\text{KNO}_3$	25	11.04 (0.02)	R1	83FSa
		0.5; $\text{NaClO}_4$	25	10.9 (0.1)	P	92GLa
	M + 2L	0.1; KCl	20	17.9 (0.1)	P	55SAa
$\text{Zn}^{2+}$	M + L	0.1; KCl	20	7.7 (0.1)	P	55SAa
		0.5; $\text{NaClO}_4$	25	7.5 (0.1)	P	92GLa
	M + 2L	0.1; KCl	20	14.1 (0.2)	P	55SAa
		0.5; $\text{NaClO}_4$	25	13.7 (0.2)	P	92GLa
$\text{Cd}^{2+}$	M + L	0.1; $\text{KNO}_3$	20	6.8 (0.2)	P	55SAa
		0.5; $\text{NaClO}_4$	25	6.4 (0.2)	P	92GLa
	M + 2L	0.5; $\text{NaClO}_4$	25	11.8 (0.2)	P	92GLa
$\text{Hg}^{2+}$	M + L	0.1; KCl	25	5.5 (0.1)	P	55SAa
	M + 2L	0.1; KCl	25	9.2 (0.1)	P	55SAa
$\text{UO}_2^{2+}$	M + L	0.1; $\text{KNO}_3$	25	9.7 (0.1)	P	70FSa

<sup>a</sup>Although MIDA has been studied since 1945 [45SKa], no values have been reported for physiological conditions ( $I = 0.15 \text{ mol L}^{-1} \text{ NaClO}_4$ ,  $37^\circ\text{C}$ ). Of the two values reported for  $35^\circ\text{C}$ , one was measured at  $I = 2.0 \text{ mol L}^{-1} \text{ KNO}_3$  [77MGb] and the other ([66KRa]) did not report experimental conditions.

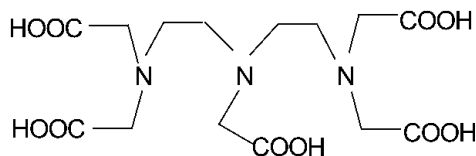
<sup>b</sup>The  $\lg K(\text{H} + \text{L})$  value for MIDA is higher than that for IDA by ca. 0.3 lg units.

<sup>c</sup>Generally, the observed trend for MIDA complexes is that they have higher stability constants than those for IDA.

<sup>d</sup>Reference [79MMf] gives reliable spectrophotometric value for  $\text{NdL}_3$  complex formation owing to a good resolution of individual absorption bands for all species:  $\lg K(\text{NdL}_3 + \text{L}) = 3.4 (0.1)$  ( $I = 0.4 \text{ mol L}^{-1} \text{ KCl}$  and "room temperature").

<sup>e</sup>See comment for IDA complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

## 7. 2,2',2'',2'''-[[[(CARBOXYMETHYL)AZANEDIYL]BIS[(ETHANE-1,2-DIYL)NITRILLO]] TETRAACETIC ACID (DIETHYLENETRIAMINEPENTAACETIC ACID), DTPA, $\text{H}_5\text{dtpa}$



Cations studied <sup>a-1</sup>:  $\text{H}^+$  <sup>a,b</sup>: 01CCa, 99SBd, 97DFa, 96GMa, 94KCa, 92DHb, 91DMc, 90ADb, 88SC, 87ZGa, 84DMb, 84ZGa, 83KDb, 82OLa, 81MPa, 80KHb, 80MIa, 79LMa, 78MGa, 77GGb, 76AMa, 76HMd, 75NAb,

74MPb, 74BAa, 74MPa, 72KIa, 72MP, 70AMa, 68CL, 68KNa, 68WRa, 67ANb, 67NKb, 65AA, 65BAc, 65RVb, 62MTc, 62SKa, 60Waa, 59AND, 59VCa, 58DRa, 55Waa

<b>Li<sup>+</sup>:</b>	60Waa	<b>Fe<sup>3+</sup>:</b>	00Bma, 97DFa,	<b>La<sup>3+</sup> i:</b>	00Cva, 98Lva, 88Mia,
<b>Mg<sup>2+</sup>:</b>	84DMb, 68CW,		90ADb, 85PLb,		87CN, 87YJa, 77CGc,
	68WRa, 65AA,		74MBa, 73KBc,		77GGb, 76Gaa,
	65WHa, 60Waa,		67Bac, 59AND,		69KA, 68CA, 65AA,
	58DRa		59VCa		62MTc, 60Hra,
<b>Ca<sup>2+</sup>:</b>	99SBd, 87ZGa,	<b>Co<sup>2+</sup>:</b>	74MBa, 68KAb, 65AA,	<b>Ce<sup>3+</sup>:</b>	88Mia, 87CN, 87YJa,
	84DMb, 84ZGa,		65WHa, 60Waa,		87ZGa, 83HPb, 82CP,
	70AMa, 68CW,		59AND, 59Cfc,		77CGc, 77GGb,
	68WRa, 65AA,	<b>Co<sup>3+</sup>:</b>	58DRa		71PVb, 71SHb, 68CL,
	65WHa, 60Hra,	<b>Ni<sup>2+</sup>:</b>	72BCb		68LFb 62MTc, 59AND
	59AND, 59Cfc,		79KNa, 78KNc,	<b>Ce<sup>4+</sup>:</b>	72Ypa, 71PMc,
	58DRa, 55Waa		74MBa, 65AA,		70MMb
<b>Sr<sup>2+</sup>:</b>	68CW, 65AA, 65WHa,		65WHa, 60Waa,	<b>Pr<sup>3+</sup>:</b>	88Mia, 87CN, 87YJa,
	62Tia, 60Waa,		59AND, 59Cfc,		82CP, 77CGc, 77GGb,
	58DRa, 55Waa		58DRa		71PRa, 70KA, 68CL,
<b>Ba<sup>2+</sup>:</b>	68CW, 65WHa, 58DRa,	<b>Cu<sup>2+</sup> g:</b>	91NBa, 85Klb, 84Hka,		62MTc, 59Hca
	60Waa, 55Waa		74BAa, 74MBa,	<b>Nd<sup>3+</sup>:</b>	88Mia, 87CN, 87YJa,
<b>Ra<sup>2+</sup>:</b>	68SKa		73KBc, 69KTc, 65AA,		84NMa, 82CP, 77CGc,
<b>Al<sup>3+</sup> c:</b>	96YHa, 80KHb, 68CA,		65WHa, 60Waa,		77GGb, 70Ktd, 68CL,
	67Abb, 66Mca		59AND, 59Cfc,		63GB, 62MTc,
<b>Ga<sup>3+</sup>:</b>	97DFa, 80KHb,		58DRa, 57HLa		59Hca, 57HLa
	76HMD, 73Nka,	<b>Zn<sup>2+</sup>:</b>	98Lva, 84DMb, 74DTa,	<b>Sm<sup>3+</sup>:</b>	88Mia, 87CN, 87YJa,
	70Caa, 67Bac,		68KA, 65AA, 65WHa,		87ZGa, 84ZGa,
	66Mca		60Hra, 60Waa,		77CGc, 77GGb,
<b>In<sup>3+</sup> d:</b>	99DLa, 97DFa, 80KHb,		59AND, 59Cfc,		76Gaa, 68CL, 63GA,
	74LKc, 72Nka,	<b>Cd<sup>2+</sup>:</b>	58DRa		62MTc, 59Hca
	67Bac, 66Zac,		84DMb, 83Ywa,	<b>Eu<sup>2+</sup>:</b>	73TKd
	63RMb		75Lwa, 74DTa, 68KA,	<b>Eu<sup>3+</sup>:</b>	97WHb, 96WHa,
<b>Tl<sup>+</sup>:</b>	79ABa, 68Kka, 67ABc		65AA, 65WHa,		88Mia, 87CN, 87YJa,
<b>Tl<sup>3+</sup> e:</b>	78VP, 67ABc, 67KAb,		60Hra, 60Waa,		87ZGa, 77CGc,
	67KA		59AND, 59Cfc,		77GGb, 76Gaa,
<b>Pb<sup>2+</sup>:</b>	93BNb, 72Lwa,		58DRa		68CL, 65Bac, 63GA,
	69Nka, 65AA,	<b>Hg<sup>2+</sup>:</b>	77GGb, 75Lba,		62MTc, 59Hca
	65WHa, 60Hra,		67Kab, 65AA,	<b>Gd<sup>3+</sup>:</b>	00SBc, 99SBd, 97BH,
	59AND		65WHa, 62MTc ,		96GMa, 94Kca,
<b>Ti<sup>IV</sup>:</b>	70KB		62SKa, 60Hra,		88Mia, 88SC, 87CN,
<b>Sb<sup>3+</sup>:</b>	71OBb, 70AMa		60Waa, 59AND		87YJa, 77CGc,
<b>Bi<sup>3+</sup> f:</b>	87Kta, 67Bac, 67NKb	<b>Ag<sup>+</sup>:</b>	68WRa, 67OA		77GGb, 69KB, 68CL,
<b>V<sup>3+</sup>:</b>	74TPa, 70KB	<b>Zr<sup>4+</sup> h:</b>	67Bac, 67Tia, 66EMd,		62MTc, 59Hca
<b>VO<sup>2+</sup>:</b>	75Nab		66Lpa, 64EMd,	<b>Tb<sup>3+</sup>:</b>	88Mia, 87CN, 77CGc,
<b>Cr<sup>3+</sup>:</b>	93BNb, 91Bma,		64PVb		77GGb, 68CL,
	91NBa, 69KC	<b>Hf<sup>4+</sup>:</b>	66EMd, 64EMd, 64PVb		62MTc, 59Hca
<b>Mn<sup>2+</sup>:</b>	84DMb, 65AA,	<b>Mo<sup>VI</sup>:</b>	71LUa	<b>Dy<sup>3+</sup>:</b>	88Mia, 87CN, 87YJa,
	65WHa, 60Hra,	<b>Pd<sup>2+</sup>:</b>	76AMa, 72KIa		77CGc, 77GGb, 68CL,
	60Waa, 59AND,	<b>Ru<sup>3+</sup>:</b>	88THa		62MTc, 59Hca
	59Cfc, 58DRa	<b>Sc<sup>3+</sup>:</b>	69KA, 68CA, 67Bac	<b>Ho<sup>3+</sup>:</b>	88Mia, 87CN, 77CGc,
<b>Mn<sup>3+</sup>:</b>	71Bph, 71Man	<b>Y<sup>3+</sup>:</b>	94Kca, 87YJa, 77CGc		77GGb, 68CL,
<b>Fe<sup>2+</sup>:</b>	00Bma, 85PLb,		77GGb, 69KA, 68CA,		62MTc, 59Hca
	65WHa, 59AND,		62MTc, 62STd,		
	59Cfc, 59VCa,		59Hca		
	58DRa				

<b>Er<sup>3+</sup></b> :	88MIa, 87CN, 77CGc, 77GGb, 68CL, 62MTc, 59HCa	<b>Th<sup>4+</sup></b> :	90SS, 89KGa, 83HPb, 76PTb, 76PAa, 75PTb, 72PA, 67BAC	<b>Cf<sup>3+</sup></b> :	71B, 66STb, 65BAC
<b>Tm<sup>3+</sup></b> :	88MIa, 87CN, 77CGc, 77GGb, 68CL, 62MTc, 59HCa	<b>UO<sub>2</sub><sup>2+</sup>j</b> :	98BMA, 90SS, 82OLA, 80KJa	<b>Cm<sup>3+</sup></b> :	72PW, 71BRa, 71MB, 71SHb, 69MOc, 68LFb, 66STb, 65BAC
<b>Yb<sup>3+</sup></b> :	89MIa, 87CN, 87YJa, 77CGc, 77GGb, 76GAa, 68CL, 62MTc, 59HCa	<b>U<sup>4+</sup> k</b> :	72PR, 68CMb	<b>Es<sup>3+</sup></b> :	65BAC
<b>Lu<sup>3+</sup></b> :	88MIa, 87CN, 77CGc, 77GGb, 69KB, 68CL, 62MTc	<b>U<sup>3+</sup></b> :	69MOc	<b>Fm<sup>3+</sup></b> :	65BAC
		<b>AmO<sub>2</sub><sup>+</sup></b> :	74NSa	<b>Pm<sup>3+</sup></b> :	68LFb
		<b>Am<sup>3+</sup> l</b> :	89RSa, 72PZ, 71BRa, 71MB, 71SHb, 69MOc, 69DBa, 68LFb, 66STb, 65BAC	<b>Np<sup>3+</sup></b> :	74KMD, 69MOc
		<b>Bk<sup>3+</sup></b> :	66STb, 65BAC	<b>Np<sup>4+</sup></b> :	73CCc, 72PB, 71EPb, 71MA, 69MOc
				<b>NpO<sub>2</sub><sup>+</sup></b> :	71MA
				<b>Pu<sup>3+</sup></b> :	78MGa, 71MB, 69MOc
				<b>Pu<sup>4+</sup></b> :	72PE, 71MA, 69MOc

*Experimental conditions of papers selected for critical evaluation:*

*I* = 0.1 mol L<sup>-1</sup> KNO<sub>3</sub>, 20 °C, Conc., gl: 79ABa, 67ANb, 67ABc, 66MCa, 62MTc  
*I* = 0.1 mol L<sup>-1</sup> KCl, 20 °C, Conc., gl, red: 59ANd, 68CMB (also, data for *I* = 0.1 mol L<sup>-1</sup> KNO<sub>3</sub>)  
*I* = 0.1 mol L<sup>-1</sup> KCl, 25 °C, Conc., luminescence: 96WHa  
*I* = 0.1 mol L<sup>-1</sup> KNO<sub>3</sub>, 25 °C, Conc., gl: 97DFa, 82OLA, 76HMD, 74BAa, 66MCa, 62MTc, 60Waa, 59CFc, 55Waa; EMF: 68WRa, 60HRA; dis: 97DFa, 59VCa  
*I* = 0.1 mol L<sup>-1</sup> Na/HClO<sub>4</sub>, 20 °C, Conc., red: 67BAC; gl: 70AMa  
*I* = 0.1 mol L<sup>-1</sup> NaClO<sub>4</sub>, 25 °C, Conc., ext: 68SKa  
*I* = 0.15 mol L<sup>-1</sup> NaClO<sub>4</sub>, 25 °C, Conc., gl, sp: 96GMa  
*I* = 0.15 mol L<sup>-1</sup> NaCl, 37 °C, Conc., gl: 91DMc, 84DMb  
*I* = 0.5 mol L<sup>-1</sup> NaClO<sub>4</sub>, 25 °C, Conc., gl: 75NAb  
*I* = 1.0 mol L<sup>-1</sup> (CH<sub>3</sub>)<sub>4</sub>NCl, 20 °C, Conc., EMF: 67ANb  
*I* = 1.0 mol L<sup>-1</sup> KCl, 25 °C, Conc., gl: 80MIa, 78MGa  
*I* = 1.0 mol L<sup>-1</sup> Na/HClO<sub>4</sub>, 20 °C, Conc., gl, sp: 91BMA, 76AMa, 67ANb; sol: 83KDb; red: 67ABc, 67BAC

**Table 3** Recommended and provisional data for DTPA.

Cation	Equilibrium	<i>I</i> /mol L <sup>-1</sup>	<i>t</i> /°C	lg <i>K</i>	Category	References
H <sup>+</sup> a,b	H + L	0.1; KNO <sub>3</sub>	20	10.58 (0.03)	R	67ANb, 62MTc
		0.1; KNO <sub>3</sub>	25	10.54 (0.03)	R	97DFa, 76HMD, 74BAa
		0.15; NaClO <sub>4</sub>	25	9.76 (0.02)	P	96GMa
		0.15; NaCl	37	9.67 (0.02)	R	91DMc, 84DMb
		1.0; (CH <sub>3</sub> ) <sub>4</sub> NCl	20	10.46 (0.03)	P	67ANb
		1.0; KCl	25	10.06 (0.03)	P	80MIa
		1.0; NaCl	20	9.48 (0.03)	P	67ANb
	HL + H	0.1; KNO <sub>3</sub>	20	8.60 (0.05)	R	74BAa, 67ANb, 62MTc
		0.1; KNO <sub>3</sub>	25	8.56 (0.01)	P	97DFa
		0.15; NaClO <sub>4</sub>	25	8.33 (0.03)	P	96GMa
		0.15; NaCl	37	8.27 (0.03)	P	84DMb
		1.0; (CH <sub>3</sub> ) <sub>4</sub> NCl	20	8.41 (0.03)	P	67ANb
		1.0; KCl	25	8.32 (0.03)	P	80MIa
		1.0; NaCl	20	8.26 (0.03)	P	67ANb

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Table 3 (Continued).

Cation	Equilibrium	<i>I</i> /mol L <sup>-1</sup>	<i>t</i> /°C	lg <i>K</i>	Category	References
	H <sub>2</sub> L + H	0.1; KNO <sub>3</sub>	20	4.30 (0.03)	R	67ANb, 62MTc
		0.1; KNO <sub>3</sub>	25	4.30 (0.03)	R	97DFa, 76HMd, 74BAa, 82OLa
		0.15; NaClO <sub>4</sub>	25	4.18 (0.03)	P	96GMa
			37	4.15 (0.03)	P	84DMb
		1.0; (CH <sub>3</sub> ) <sub>4</sub> NCl	20	4.14 (0.03)	P	67ANb
		1.0; KCl	25	4.13 (0.03)	P	80MIa
		1.0; NaCl	20	4.19 (0.03)	P	67ANb
		H <sub>3</sub> L + H	0.1; KNO <sub>3</sub>	20	2.58 (0.03)	R
	25			2.77 (0.05)	R	97DFa, 76HMd
	0.15; NaClO <sub>4</sub>		25	2.68 (0.03)	P	96GMa
37			2.68 (0.03)	P	84DMb	
1.0; (CH <sub>3</sub> ) <sub>4</sub> NCl	20		2.7 (0.1)	P	67ANb	
1.0; KCl	25		2.5 (0.1)	P	80MIa	
1.0; NaCl	20		2.5 (0.1)	P	67ANb	
H <sub>4</sub> L + H	0.1; KNO <sub>3</sub>	20	1.8 (0.1)	P	62MTc	
		25	2.0 (0.1)	R	76HMd, 68WRa	
	0.15; NaClO <sub>4</sub>	25	2.0 (0.1)	P	96GMa	
		37	2.1 (0.1)	P	84DMb	
	1.0; (CH <sub>3</sub> ) <sub>4</sub> NCl	20	2.2 (0.1)	P	67ANb	
	1.0; KCl	25	2.3 (0.1)	P	80MIa	
	1.0; NaCl	20	1.9 (0.1)	P	83KDb	
H <sub>5</sub> L + H	1.0; Na/HClO <sub>4</sub>	20	1.2 (0.2)	P	83KDb	
	1.0; K/HCl	25	1.7 (0.2)	P	80MIa	
H <sub>6</sub> L + H	1.0; Na/HClO <sub>4</sub>	20	0.8 (0.2)	P	83KDb	
	1.0; K/HCl	25	0.9 (0.2)	P	80MIa	
Li <sup>+</sup>	M + L	0.1; KNO <sub>3</sub>	25	3.1 (0.2)	P	60WAa
Mg <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	25	9.3 (0.1)	R	68WRa, 60WAa
		0.15; NaCl	37	8.56 (0.05)	P	84DMb
	ML + H	0.1; KNO <sub>3</sub>	25	6.9 (0.1)	P	60WAa
		0.15; NaCl	37	6.96 (0.05)	P	84DMb
	MHL + H	0.15; NaCl	37	4.68 (0.05)	P	84DMb
	MH <sub>2</sub> L + H	0.15; NaCl	37	3.74 (0.05)	P	84DMb
	ML + M	0.15; NaCl	37	2.07 (0.05)	P	84DMb
Ca <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	25	10.7 (0.1)	R	68WRa, 60HRa, 59CFc, 55WAa
		0.1; NaClO <sub>4</sub>	20	10.8 (0.1)	P	70AMa, 59ANd
		0.15; NaCl	37	9.8 (0.1)	P	84DMb
	ML + H	0.1; NaNO <sub>3</sub>	20	6.10 (0.05)	P	59ANd
		0.1; KNO <sub>3</sub>	25	6.10 (0.05)	P	59CFc
		0.15; NaCl	37	6.00 (0.05)	P	84DMb
		0.15; NaCl	37	4.40 (0.05)	P	84DMb
	MHL + H	0.15; NaCl	37	4.40 (0.05)	P	84DMb
	MH <sub>2</sub> L + H	0.15; NaCl	37	3.70 (0.05)	P	84DMb
	ML + M	0.1; NaNO <sub>3</sub>	20	2.0 (0.1)	P	59ANd
		0.1; NaNO <sub>3</sub>	37	2.1 (0.1)	P	84DMb

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**Table 3** (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
$\text{Sr}^{2+}$	M + L	0.1; $\text{KNO}_3$	25	9.7 (0.1)	P	60WAa, 55WAa
$\text{Ba}^{2+}$	M + L	0.1; $\text{KNO}_3$	25	8.8 (0.1)	P	60WAa, 55WAa
$\text{Ra}^{2+}$	M + L	0.1; $\text{NaClO}_4$	25	8.5 (0.1)	P	68SKa
$\text{Al}^{3+ \text{ c}}$	M + L	0.1; $\text{KNO}_3$	20	18.4 (0.1)	P	66MCa
		0.1; $\text{KNO}_3$	25	18.5 (0.1)	P	66MCa
	ML + H	0.1; $\text{KNO}_3$	20	4.6 (0.1)	P	66MCa
$\text{Ga}^{3+}$	M + L	0.1; $\text{NaClO}_4$	20	25.5 (0.1)	P	67BAc
		0.1; $\text{KNO}_3$	25	25.1 (0.1)	P	97DFa
	ML + H	0.1; $\text{NaClO}_4$	20	4.35 (0.05)	P	67BAc
		0.1; $\text{KNO}_3$	25	4.10 (0.05)	R	97DFa, 76HMd
	MHL + H	0.1; $\text{KNO}_3$	25	1.8 (0.1)	P	97DFa
	ML + OH	0.1; $\text{NaClO}_4$	20	6.52 (0.05)	P	67BAc
$\text{In}^{3+ \text{ d}}$	ML + OH	0.1; $\text{Na/KClO}_4$	20	2.06 (0.05)	P	67BAc
$\text{Tl}^+$	M + L	0.1; $\text{KNO}_3$	20	5.97 (0.05)	R1	79ABa, 67ABc
	ML + H	0.1; $\text{KNO}_3$	20	8.8 (0.1)	P	79ABa
$\text{Tl}^{3+ \text{ e}}$	M(OH)L + H	1.0; $\text{NaClO}_4$	20	10.9 (0.1)	P	67ABc
$\text{Pb}^{2+}$	M + L	0.1; $\text{NaNO}_3$	20	18.9 (0.1)	P	59ANd
	ML + H	0.1; $\text{NaNO}_3$	20	4.52 (0.05)	P	59ANd
	ML + M	0.1; $\text{NaNO}_3$	20	3.41 (0.05)	P	59ANd
$\text{Sb}^{3+}$	ML + H	0.1; $\text{NaClO}_4$	20	3.57 (0.05)	P	70AMa
	ML + 2OH	0.1; $\text{NaClO}_4$	20	9.82 (0.05)	P	70AMa
$\text{Bi}^{3+ \text{ f}}$	ML + H	1.0; $\text{NaClO}_4$	20	2.6 (0.1)	P	67BAc
	ML + OH	1.0; $\text{NaClO}_4$	20	2.7 (0.1)	P	67BAc
$\text{VO}^{2+}$	M + L	0.5; $\text{NaClO}_4$	25	16.3 (0.2)	P	75NAb
	ML + H	0.5; $\text{NaClO}_4$	25	7.0 (0.1)	P	75NAb
	2M + L	0.5; $\text{NaClO}_4$	25	23.3 (0.2)	P	75NAb
$\text{Cr}^{3+}$	M + L	1.0; $\text{Na/HClO}_4$	20	22.1 (0.1)	P	91BMa
	ML + H	1.0; $\text{Na/HClO}_4$	20	7.65 (0.05)	P	91BMa
	MHL + H	1.0; $\text{Na/HClO}_4$	20	6.15 (0.05)	P	91BMa
	$\text{MH}_2\text{L} + \text{H}$	1.0; $\text{Na/HClO}_4$	20	2.85 (0.05)	P	91BMa
	$\text{MH}_3\text{L} + \text{H}$	1.0; $\text{Na/HClO}_4$	20	1.50 (0.1)	P	91BMa
$\text{Mn}^{2+}$	M + L	0.1; $\text{NaNO}_3$	20	15.6 (0.1)	P	59ANd
		0.1; $\text{KNO}_3$	25	15.5 (0.1)	R	60HRa, 60WAa
		0.15; $\text{NaCl}$	37	14.3 (0.1)	P	84DMb
	ML + H	0.1; $\text{NaNO}_3$	20	4.03 (0.05)	P	59ANd
	ML + M	0.1; $\text{NaNO}_3$	20	2.1 (0.1)	P	59ANd
	$\text{Fe}^{2+}$	M + L	0.1; $\text{NaNO}_3$	20	16.0 (0.1)	P
ML + H		0.1; $\text{NaNO}_3$	20	5.32 (0.05)	R1	59CFc
		0.1; $\text{KNO}_3$	25	5.30 (0.05)	R1	59ANd
ML + M		0.1; $\text{NaNO}_3$	20	3.0 (0.1)	P	59ANd

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Table 3 (Continued).

Cation	Equilibrium	<i>I</i> /mol L <sup>-1</sup>	<i>t</i> /°C	lg <i>K</i>	Category	References
Fe <sup>3+</sup>	M + L	0.1; NaClO <sub>4</sub>	20	27.3 (0.2)	P	67BAc
		0.1; KNO <sub>3</sub>	25	27.8 (0.1)	P	97DFa
	ML + H	0.1; NaClO <sub>4</sub>	20	3.58 (0.05)	R1	67BAc
		0.1; KNO <sub>3</sub>	25	3.56 (0.05)	R1	59VCa
	ML + OH	0.1; NaClO <sub>4</sub>	20	3.9 (0.1)	R1	67BAc
		0.1; KNO <sub>3</sub>	25	4.1 (0.1)	R1	59VCa
Co <sup>2+</sup>	M + L	0.1; NaNO <sub>3</sub>	20	19.3 (0.1)	P	59ANd
	ML + H	0.1; NaNO <sub>3</sub>	20	4.72 (0.05)	P	59ANd
	ML + M	0.1; NaNO <sub>3</sub>	20	3.5 (0.1)	P	59ANd
Ni <sup>2+</sup>	M + L	0.1; NaNO <sub>3</sub>	20	20.2 (0.1)	P	59ANd
		0.1; KNO <sub>3</sub>	25	20.1 (0.1)	P	60WAa, 59CFc
	ML + H	0.1; NaNO <sub>3</sub>	20	5.62 (0.05)	P	59ANd
		0.1; KNO <sub>3</sub>	25	5.6 (0.1)	P	60WAa, 59CFc
	ML + M	0.1; NaNO <sub>3</sub>	20	5.4 (0.1)	P	59ANd
		0.1; KNO <sub>3</sub>	25	5.6 (0.1)	P	60WAa, 59CFc
Cu <sup>2+</sup> g	M + L	0.1; NaNO <sub>3</sub>	20	21.5 (0.1)	P	59ANd
		0.1; KClO <sub>4</sub>	25	21.5 (0.1)	P	74BAa
	ML + H	0.1; NaNO <sub>3</sub>	20	4.74 (0.02)	R1	59ANd
		0.1; KNO <sub>3</sub> /ClO <sub>4</sub>	25	4.79 (0.02)	R	74BAa, 59CFc
	MHL + H	0.1; KClO <sub>4</sub>	25	2.88 (0.05)	P	74BAa
	ML + M	0.1; NaNO <sub>3</sub>	20	5.5 (0.1)	P	59ANd
Zn <sup>2+</sup>	M + L	0.1; NaNO <sub>3</sub>	20	18.6 (0.1)	P	59ANd
		0.15; NaCl	37	17.45 (0.05)	P	84DMb
	ML + H	0.1; NaNO <sub>3</sub>	20	5.43 (0.05)	P	59ANd
		0.15; NaCl	37	5.08 (0.05)	P	84DMb
	MHL + H	0.15; NaCl	37	2.35 (0.05)	P	84DMb
	ML + M	0.1; NaNO <sub>3</sub>	20	4.4 (0.1)	P	59ANd
Cd <sup>2+</sup>	M + L	0.1; NaNO <sub>3</sub>	20	19.3 (0.1)	P	59ANd
		0.15; NaCl	37	17.76 (0.05)	P	84DMb
	ML + H	0.1; NaNO <sub>3</sub>	20	4.06 (0.05)	P	59ANd
		0.15; NaCl	37	3.77 (0.05)	P	84DMb
	MHL + H	0.15; NaCl	37	2.79 (0.05)	P	84DMb
	ML + M	0.1; NaNO <sub>3</sub>	20	3.0 (0.1)	P	59ANd
Hg <sup>2+</sup>	M + L	0.1; NaNO <sub>3</sub>	20	26.7 (0.1)	R	59ANd, 62MTc
	ML + H	0.1; NaNO <sub>3</sub>	20	4.2 (0.1)	R	59ANd, 62MTc
Ag <sup>+</sup>	M + L	0.1; KNO <sub>3</sub>	25	8.7 (0.1)	P	68WRa
Zr <sup>4+</sup> h	ML + OH	1.0; NaClO <sub>4</sub>	20	8.1 (0.1)	P	67BAc
Pd <sup>2+</sup>	M + L	1.0; HClO <sub>4</sub>	20	29.7 (0.1)	R1	76AMa
	ML + H	1.0; NaClO <sub>4</sub>	20	3.49 (0.05)	R1	76AMa
	MHL + H	1.0; NaClO <sub>4</sub>	20	2.9 (0.1)	P	76AMa
	MH <sub>2</sub> L + H	1.0; NaClO <sub>4</sub>	20	2.6 (0.1)	P	76AMa
	MH <sub>3</sub> L + H	1.0; NaClO <sub>4</sub>	20	1.9 (0.1)	P	76AMa
Eu <sup>3+</sup> i	M + L	0.1; KNO <sub>3</sub>	25	22.4 (0.1)	P	96WHa, 62MTc
Gd <sup>3+</sup> i	M + L	0.1; KNO <sub>3</sub>	25	22.5 (0.1)	P	62MTc

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**Table 3** (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
Th <sup>4+</sup>	M + L	0.1; NaClO <sub>4</sub>	20	28.8 (0.1)	P	67BAc
	ML + H	0.1; NaClO <sub>4</sub>	20	2.16 (0.05)	P	67BAc
	ML + OH	0.1; NaClO <sub>4</sub>	20	4.9 (0.2)	P	67BAc
UO <sub>2</sub> <sup>2+</sup> j	M + HL	0.1; KNO <sub>3</sub>	25	8.8 (0.2)	P	82OLa
U <sup>4+</sup> k	ML(OH) + H	0.1; KCl	25	7.8 (0.1)	P	68CMb

<sup>a</sup>The reaction enthalpy for DTPA protonation  $\Delta_r H_c$  ( $H_n L + H$ ) is exothermic for  $n = 0$  or  $1$  and endothermic for  $n = 3$  or  $4$  [74MPb, 62MTc]. The general trend is therefore a decrease in  $\lg K(L + H)$  and  $\lg K(HL + H)$  with an increase of temperature, with the opposite trend for  $\lg K(H_3L + H)$  and  $\lg K(H_4L + H)$ .

<sup>b</sup>Values for DTPA protonation  $L + nH$  ( $n = 1$  and  $2$ ) are strongly dependent on the concentration and nature of the background cation owing to complex formation with Na<sup>+</sup> and K<sup>+</sup>. For  $n > 2$ , as well as for  $\lg K(ML + H)$ , the influence of the background cation's nature is negligible. Although [97CS] gives a stability constant for K<sup>+</sup> ( $\lg K_{KL} = 3.1$ ) the original reference was not found by the reviewers. But the same value is reported for the DTPA complex with Li<sup>+</sup> ( $\lg K_{LiL} = 3.1$ ) [60WAA].

<sup>c</sup>Unlike most other cations the formation of the Al<sup>III</sup>-DTPA complex has a positive  $\Delta_r H_c$ . The values given by [66MCA] for 25 °C and 20 °C are consistent with this. The value  $\lg K(AlL + OH) = 6.6$  (0.5) [67ABb] is considered reliable (0.1 mol L<sup>-1</sup> KNO<sub>3</sub>, 25 °C).

<sup>d</sup>A critical evaluation of In<sup>III</sup> stability constants [83TU] reports the mean  $\lg K(In + L) = 28.4$  (0.8) from three determinations: 29.0, 27.65 and 28.42 [67BAc, 63RMB, 66ZAc], and evaluates this value as doubtful. Later research [99DLA] based on spectrophotometric titration of the In<sup>III</sup>-HBED-DTPA system in 0.5 mol L<sup>-1</sup> Me<sub>4</sub>NCl at 25 °C reported  $\lg K(In + L) = 31.17$  (0.02). This value is higher than  $\lg K_{ML}$  for In<sup>III</sup>-HBED and is assigned an unrealistic precision as some important experimental details are missing (e.g.,  $\lg K(L + nH)$  values of DTPA for 0.5 mol L<sup>-1</sup> Me<sub>4</sub>NCl at 25 °C). Nevertheless it supports indirectly the stability constant obtained in [67BAc] ( $\lg K_{InL} = 29.0$  for 0.1 mol L<sup>-1</sup> NaClO<sub>4</sub>, 25 °C), which is lower owing to electrolyte cation (Na/KClO<sub>4</sub>) competition. Another recent publication based on the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox equilibrium gives  $\lg K(In + L) = 29.48$  (0.04) [97DFa] for 0.1 mol L<sup>-1</sup> KNO<sub>3</sub> and 25 °C. Thus, the value  $\lg K(M + L) = 29.3$  (0.5) (0.1 mol L<sup>-1</sup> Na/KClO<sub>4</sub>, 25 °C) [97DFa, 67BAc] is considered the most reliable to date.

<sup>e</sup>For Ti<sup>3+</sup> [67ABc] gives an estimate of  $\lg K(M + L) = 46$  (1) (1.0 mol L<sup>-1</sup> NaClO<sub>4</sub>, 20 °C), which is considered the most reliable among data published, although far outside the "Provisional" range.

<sup>f</sup>For Bi<sup>3+</sup> [67BAc] gives an estimate of  $\lg K(M + L) = 36$  (1) (1.0 mol L<sup>-1</sup> NaClO<sub>4</sub>, 20 °C), which is considered the most reliable among data published.

<sup>g</sup> $\lg K(CuH_2L + H) = 2.1$  (0.3) [85KLb] at  $I = 0.1$  mol L<sup>-1</sup> NaCl and 25 °C is considered to be reliable.

<sup>h</sup>For Zr<sup>4+</sup>, [67BAc] gives an estimate of  $\lg K(M + L) = 37$  (1) (1.0 mol L<sup>-1</sup> NaClO<sub>4</sub>, 20 °C), which is considered the most reliable among data published.

<sup>i</sup>For the rare earths, the sequence reported by [62MTc] (0.1 mol L<sup>-1</sup> KNO<sub>3</sub>, 25 °C, Conc.), is recommended as **Provisional**:

Ln <sup>3+</sup>	$\lg K(M + L)$	Ln <sup>3+</sup>	$\lg K(M + L)$
La <sup>3+</sup>	19.48 (0.08)	Tb <sup>3+</sup>	22.71 (0.08)
Ce <sup>3+</sup>	20.5 (0.2)	Dy <sup>3+</sup>	22.82 (0.08)
Pr <sup>3+</sup>	21.07 (0.08)	Ho <sup>3+</sup>	22.78 (0.08)
Nd <sup>3+</sup>	21.6 (0.08)	Er <sup>3+</sup>	22.74 (0.08)
Sm <sup>3+</sup>	22.34 (0.08)	Tm <sup>3+</sup>	22.72 (0.08)
Eu <sup>3+</sup>	22.39 (0.08)	Yb <sup>3+</sup>	22.62 (0.08)
Gd <sup>3+</sup>	22.46 (0.08)	Lu <sup>3+</sup>	22.44 (0.08)

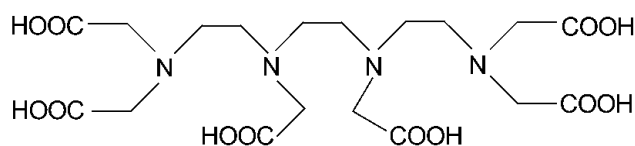
<sup>j</sup>In the report for UO<sub>2</sub><sup>2+</sup> [82OLa]  $\lg K(H + L)$  and  $\lg K(HL + H)$  values used were both 0.1 log units lower than the recommended ones, thus the originally reported stability constants  $\lg K(2M + L) = 19.0$  (0.4);  $\lg K(2M + HL) = 13.4$  (0.3) will be an underestimate by ca. 0.2 log units. Within this precision, these data are treated as reliable:  $\lg K(2M + L) = 19.2$  (0.6);  $\lg K(2M + HL) = 13.5$  (0.5).

<sup>k</sup> $\lg K(U^{IV} + L)$  can be estimated as ca. 30.9 [72PR] if one uses the data of [67BAc] for Th<sup>IV</sup>, and the relative stability for U<sup>IV</sup> and Th<sup>IV</sup> complexes as reported in [72PR] for  $I = 0.1 - 0.5$  mol L<sup>-1</sup> and 20 °C.

<sup>l</sup> $\lg K(AM^{III} + L) = 23.0$  (0.5) reported by [65BAc] (0.1 mol L<sup>-1</sup> NH<sub>4</sub>ClO<sub>4</sub>, 25 °C, ix) is accepted as realistic, although it will be an underestimate owing to oversight of H<sub>6</sub>dtpa<sup>+</sup> formation within the pH range 2.2–2.7.



**8. 3,6,9,12-TETRAKIS(CARBOXYMETHYL)-3,6,9,12-TETRAAZATETRADECANEDIOIC ACID (TRIETHYLENETETRAMINEHEXAACETIC ACID), TTHA, H<sub>6</sub>ttha**



*Cations studied:* **H<sup>+</sup>**<sup>a</sup>: 00CLa, 98ACc, 98AKa, 97DFa, 82OLa, 80KHb, 80MMd, 79LMa, 76HMd, 76NAa, 71LUa, 70LAd, 69ALb, 65BMf, 63GHa, 56FRa

<b>Na<sup>+</sup></b> <sup>a</sup> :	80KNa	<b>Fe<sup>3+</sup></b> <sup>j</sup> :	97DFa, 70HAa, 67BMa, 65SCb	<b>Mo<sup>VI</sup></b> <sup>t</sup> :	71LUa
<b>Mg<sup>2+</sup></b> <sup>b</sup> :	70HAa, 67BMd, 65BMf, 63GHa	<b>Co<sup>2+</sup></b> <sup>k,l</sup> :	70HAa, 68SCa, 65BMf	<b>La<sup>3+</sup></b> :	00CVa, 98AKa, 76GAa, 75AA, 70HAa, 69YMa, 65BMf
<b>Ca<sup>2+</sup></b> :	69ALb, 65BMf, 63GHa	<b>Co<sup>3+</sup></b> <sup>m</sup> :	69BHb	<b>Ce<sup>3+</sup></b> <sup>u</sup> :	69HGa
<b>Sr<sup>2+</sup></b> :	63GHa	<b>Ni<sup>2+</sup></b> <sup>k,n</sup> :	70HAa, 68SCa, 67BMd, 65BMf	<b>Pr<sup>3+</sup></b> :	75AA
<b>Ba<sup>2+</sup></b> :	63GHa	<b>Cu<sup>2+</sup></b> <sup>k,o</sup> :	70HAa, 69ALb, 67BMd, 67BMa, 65BMf, 65KKA	<b>Nd<sup>3+</sup></b> :	75AA, 70HAa, 69YMa
<b>Al<sup>3+</sup></b> <sup>c</sup> :	98ACa, 80KHb, 70HAa	<b>Zn<sup>2+</sup></b> :	71NK, 71YMb, 70HAa, 70LAd, 69ALb, 69LUa, 68SCa	<b>Sm<sup>3+</sup></b> :	75AA, 69LUa, 68SCa
<b>Ga<sup>3+</sup></b> :	98ACa, 98AKa, 97DFa, 80KHb, 80MMd, 76HMd, 69YMa	<b>Cd<sup>2+</sup></b> <sup>p</sup> :	88HPa, 81MNa, 71YMb, 70HAa, 69LUa, 68SCa, 65CKa	<b>Eu<sup>3+</sup></b> :	75AA, 76GAa,
<b>In<sup>3+</sup></b> <sup>d</sup> :	97DFa, 84Tmc	<b>Hg<sup>2+</sup></b> <sup>q,r</sup> :	90AC, 70HAa, 70LAd, 69YMa, 66SCb	<b>Gd<sup>3+</sup></b> :	75AA
<b>Tl<sup>+</sup></b> :	77CNa	<b>Ag<sup>+</sup></b> :	72RHb, 68WRa	<b>Tb<sup>3+</sup></b> :	75AA
<b>Tl<sup>3+</sup></b> <sup>e</sup> :	00CLa	<b>Zr<sup>4+</sup></b> <sup>s</sup> :	96YHa, 66ENc	<b>Dy<sup>3+</sup></b> :	75AA
<b>Pb<sup>2+</sup></b> <sup>f</sup> :	88HPa, 71YMb, 70HAa, 69LUa, 68SCa	<b>Hf<sup>4+</sup></b> :	96YHa, 66ENc	<b>Ho<sup>3+</sup></b> :	75AA, 69YMa
<b>Bi<sup>3+</sup></b> <sup>g</sup> :	79NPa, 69YMa			<b>Er<sup>3+</sup></b> :	70HAa
<b>VO<sup>2+</sup></b> <sup>h</sup> :	76NAa			<b>Tm<sup>3+</sup></b> :	75AA
<b>Mn<sup>2+</sup></b> :	98AKa, 70HAa			<b>Yb<sup>3+</sup></b> :	76GAa, 75AA
<b>Fe<sup>2+</sup></b> <sup>i</sup> :	65SCb			<b>Th<sup>4+</sup></b> <sup>v</sup> :	85MSc, 70HAa, 65BMf
				<b>U<sup>4+</sup></b> :	68CMb
				<b>UO<sub>2</sub><sup>2+</sup></b> :	82Nac, 82OLa
				<b>Am<sup>3+</sup></b> <sup>w</sup> :	69DBa

*Experimental conditions of papers selected for critical evaluation:*

*I* = 0.1 mol L<sup>-1</sup> KNO<sub>3</sub>, 20 °C, Conc., gl: 70LAd, 69ALb

*I* = 0.1 mol L<sup>-1</sup> KNO<sub>3</sub>, 25 °C, Conc., gl: 98AKa, 97DFa, 90AC, 82OLa, 79LMa, 75AA, 76HMd, 70HAa, 69BHb, 69LUa, 69YMa, 68Cmb, 68WRa, 65BMf

*I* = 0.1 mol L<sup>-1</sup> KCl, 30 °C, Conc., gl: 63GHa

*I* = 0.1 mol L<sup>-1</sup> Me<sub>4</sub>NNO<sub>3</sub>, 25 °C, Conc., red: 98ACc

*I* = 0.5 mol L<sup>-1</sup> NaClO<sub>4</sub>, 25 °C, Conc., gl: 76NAa, 77CNa

*I* = 0.5 mol L<sup>-1</sup> Na/KNO<sub>3</sub>, 25 °C, Conc., kin: 80KNa

*I* = 1.0 mol L<sup>-1</sup> NaClO<sub>4</sub>, 25 °C, Conc., gl: 00CLa

*I* = 1.0 mol L<sup>-1</sup> NaNO<sub>3</sub>, 25 °C, Conc., gl: 00CLa

**Table 4** Recommended and provisional data for TTHA.

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
H <sup>+</sup> <sup>a,b</sup>	H + L	0.1; KNO <sub>3</sub>	20	10.65 (0.03)	R1	69ALb
		0.1; KNO <sub>3</sub>	25	10.62 (0.02)	R	98AKa, 97DFa, 79LMa, 76HMd
		0.1; Me <sub>4</sub> NNO <sub>3</sub>	25	10.63 (0.05)	R1	98ACc
		0.5; NaClO <sub>4</sub>	25	9.73 (0.05)	P	76NAa
		1.0; NaClO <sub>4</sub>	25	9.43 (0.03)	R1	00CLa
		1.0; NaNO <sub>3</sub>	25	9.39 (0.02)	R1	00CLa
	HL + H	0.1; KNO <sub>3</sub>	20	9.54 (0.03)	R1	69ALb
		0.1; KNO <sub>3</sub>	25	9.54 (0.03)	R	98AKa, 97DFa, 79LMa, 76HMd
		0.1; Me <sub>4</sub> NNO <sub>3</sub>	25	9.46 (0.02)	R1	98ACc
		0.5; NaClO <sub>4</sub>	25	8.76 (0.05)	P	76NAa
		1.0; NaClO <sub>4</sub>	25	8.69 (0.03)	R1	00CLa
		1.0; NaNO <sub>3</sub>	25	8.74 (0.03)	R1	00CLa
	H <sub>2</sub> L + H	0.1; KNO <sub>3</sub>	20	6.10 (0.02)	R1	69ALb
		0.1; KNO <sub>3</sub>	25	6.15 (0.03)	R	98AKa, 97DFa, 79LMa, 76HMd
		0.1; Me <sub>4</sub> NNO <sub>3</sub>	25	6.11 (0.03)	R1	98ACc
		0.5; NaClO <sub>4</sub>	25	5.92 (0.05)	P	76NAa
		1.0; NaClO <sub>4</sub>	25	6.00 (0.03)	R1	00CLa
		1.0; NaNO <sub>3</sub>	25	5.88 (0.03)	R1	00CLa
	H <sub>3</sub> L + H	0.1; KNO <sub>3</sub>	20	4.03 (0.04)	P	69ALb
		0.1; KNO <sub>3</sub>	25	4.07 (0.03)	R	98AKa, 97DFa, 79LMa, 76HMd
		0.1; Me <sub>4</sub> NNO <sub>3</sub>	25	4.04 (0.04)	R1	98ACc
		0.5; NaClO <sub>4</sub>	25	3.94 (0.05)	P	76NAa
		1.0; NaClO <sub>4</sub>	25	3.99 (0.05)	P	00CLa
		1.0; NaNO <sub>3</sub>	25	3.97 (0.03)	P	00CLa
	H <sub>4</sub> L + H	0.1; KNO <sub>3</sub>	20	2.7 (0.1)	P	69ALb
		0.1; KNO <sub>3</sub>	25	2.79 (0.07)	P	98AKa, 97DFa, 79LMa, 76HMd
		0.1; Me <sub>4</sub> NNO <sub>3</sub>	25	2.75 (0.04)	R1	98ACc
		0.5; NaClO <sub>4</sub>	25	2.8 (0.1)	P	76NAa
		1.0; NaClO <sub>4</sub>	25	2.7 (0.1)	P	00CLa
		1.0; NaNO <sub>3</sub>	25	2.6 (0.1)	P	00CLa
	H <sub>5</sub> L + H	0.1; KNO <sub>3</sub>	20	2.3 (0.1)	P	69ALb
		0.1; KNO <sub>3</sub>	25	2.2 (0.1)	P	98AKa, 97DFa, 79LMa, 76HMd
		0.1; Me <sub>4</sub> NNO <sub>3</sub>	25	2.34 (0.07)	R1	98ACc
0.5; NaClO <sub>4</sub>		25	2.3 (0.1)	P	76NAa	
1.0; NaClO <sub>4</sub>		25	2.3 (0.1)	P	00CLa	
	1.0; NaNO <sub>3</sub>	25	2.2 (0.1)	P	00CLa	
H <sub>6</sub> L + H	0.1; KNO <sub>3</sub>	25	1.8 (0.1)	P	98AKa, 79LMa	
H <sub>7</sub> L + H	0.1; KNO <sub>3</sub>	25	1.5 (0.1)	P	98AKa, 79LMa	

*(continues on next page)*

Table 4 (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
Na <sup>+</sup>	M + L	0.5; Na/KNO <sub>3</sub>	25	1.0 (0.2)	P	80KNa
Mg <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	25	8.5 (0.1)	P	70HAa, 65BMf
	ML + H	0.1; KNO <sub>3</sub>	25	9.3 (0.1)	P	70HAa, 65BMf
	MHL + H	0.1; KNO <sub>3</sub>	25	4.7 (0.1)	P	65BMf
	ML + M	0.1; KNO <sub>3</sub>	25	5.9 (0.1)	P	70HAa
Ca <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	20	10.5 (0.1)	P	69ALb
	ML + H	0.1; KNO <sub>3</sub>	20	8.4 (0.1)	P	69ALb
	MHL + H	0.1; KNO <sub>3</sub>	20	4.8 (0.1)	P	69ALb
	ML + M	0.1; KNO <sub>3</sub>	20	4.2 (0.1)	P	69ALb
Sr <sup>2+</sup>	M + L	0.1; KCl	30	9.3 (0.1)	P	63GHa
	ML + H	0.1; KCl	30	7.8 (0.1)	P	63GHa
	MHL + H	0.1; KCl	30	2.6 (0.1)	P	63GHa
	ML + M	0.1; KCl	30	3.5 (0.1)	P	63GHa
Ba <sup>2+</sup>	M + L	0.1; KCl	30	8.2 (0.1)	P	63GHa
	ML + H	0.1; KCl	30	7.7 (0.1)	P	63GHa
	MHL + H	0.1; KCl	30	3.7 (0.1)	P	63GHa
	ML + M	0.1; KCl	30	3.4 (0.1)	P	63GHa
Al <sup>3+</sup>	ML + H	0.1; K/Me <sub>4</sub> NNO <sub>3</sub>	25	5.9 (0.1)	P	98ACa, 70HAa
Ga <sup>3+</sup>	M + L	0.1; K/Me <sub>4</sub> NNO <sub>3</sub>	25	27.7 (0.2)	P	98ACa, 98AKa, 97DFa
	ML + H	0.1; K/Me <sub>4</sub> NNO <sub>3</sub>	25	5.1 (0.2)	P	98ACa, 98AKa
	MHL + H	0.1; K/Me <sub>4</sub> NNO <sub>3</sub>	25	4.0 (0.2)	P	98ACa, 98AKa
	M(OH)L + H	0.1; K/Me <sub>4</sub> NNO <sub>3</sub>	25	9.4 (0.2)	P	98ACa, 98AKa, 97DFa
In <sup>3+</sup>	ML + H	0.1; KNO <sub>3</sub>	25	7.3 (0.2)	P	97DFa
Tl <sup>+</sup>	M + L	0.5; NaClO <sub>4</sub>	25	4.9 (0.1)	P	77CNa
	ML + H	0.5; NaClO <sub>4</sub>	25	9.7 (0.1)	P	77CNa
Tl <sup>3+</sup>	ML + H	1.0; NaClO <sub>4</sub>	25	5.1 (0.2)	P	00CLa
Pb <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	25	18.0 (0.2)	P	70HAa, 69LUa
	ML + H	0.1; KNO <sub>3</sub>	25	6.1 (0.2)	P	70HAa, 69LUa
	ML + M	0.1; KNO <sub>3</sub>	25	11.0 (0.2)	P	70HAa, 69LUa
Mn <sup>2+</sup>	M + L	0.1; KNO <sub>3</sub>	25	14.7 (0.2)	P	98AKa, 70HAa
	ML + H	0.1; KNO <sub>3</sub>	25	9.0 (0.2)	P	98AKa, 70HAa
	MHL + H	0.1; KNO <sub>3</sub>	25	3.5 (0.2)	P	98AKa, 70HAa
	MH <sub>2</sub> L + H	0.1; KNO <sub>3</sub>	25	2.8 (0.2)	P	98AKa, 70HAa
	ML + M	0.1; KNO <sub>3</sub>	25	6.3 (0.2)	P	98AKa, 70HAa
Fe <sup>3+</sup>	ML + H	0.1; KNO <sub>3</sub>	25	7.5 (0.2)	P	97DFa, 70HAa
Co <sup>2+</sup>	ML + H	0.1; KNO <sub>3</sub>	25	8.2 (0.2)	P	70HAa
	M <sub>2</sub> L + H	0.1; KNO <sub>3</sub>	25	3.0 (0.2)	P	70HAa
	M <sub>2</sub> HL + H	0.1; KNO <sub>3</sub>	25	2.6 (0.2)	P	70HAa
Ni <sup>2+</sup>	ML + H	0.1; KNO <sub>3</sub>	25	8.0 (0.2)	P	70HAa
	M <sub>2</sub> L + H	0.1; KNO <sub>3</sub>	25	2.6 (0.2)	P	70HAa

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**Table 4** (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
$\text{Cu}^{2+}$	ML + H	0.1; $\text{KNO}_3$	25	8.00 (0.05)	R	70HAa, 69ALb
	ML + M	0.1; $\text{KNO}_3$	25	13.5 (0.1)	P	70HAa, 69ALb
	$\text{M}_2\text{L} + \text{H}$	0.1; $\text{KNO}_3$	25	3.0 (0.2)	P	70HAa, 69ALb
	$\text{M}_2\text{HL} + \text{H}$	0.1; $\text{KNO}_3$	25	2.7 (0.2)	P	70HAa, 69ALb
$\text{Zn}^{2+}$	M + L	0.1; $\text{KNO}_3$	25	18.1 (0.2)	P	70LAd, 69ALb
	ML + H	0.1; $\text{KNO}_3$	25	8.1 (0.2)	P	70LAd, 69ALb
$\text{Cd}^{2+}$	M + L	0.1; $\text{KNO}_3$	25	18.7 (0.2)	P	70HAa
	ML + H	0.1; $\text{KNO}_3$	25	8.3 (0.2)	P	70HAa
	MHL + H	0.1; $\text{KNO}_3$	25	3.2 (0.3)	P	70HAa
	ML + M	0.1; $\text{KNO}_3$	25	8.2 (0.3)	P	70HAa
$\text{Hg}^{2+}$	M+L	0.1; $\text{KNO}_3$	25	28.1 (0.2)	P	90AC, 70HAa
	ML+H	0.1; $\text{KNO}_3$	25	6.2 (0.2)	P	90AC, 70HAa
	ML+M	0.1; $\text{KNO}_3$	25	13.8 (0.2)	P	90AC, 70HAa
$\text{Ag}^+$	M + L	0.1; $\text{KNO}_3$	25	8.7 (0.2)	P	68WRa
	ML + H	0.1; $\text{KNO}_3$	25	9.1 (0.2)	P	68WRa
	ML + M	0.1; $\text{KNO}_3$	25	5.2 (0.2)	P	68WRa
$\text{La}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	3.2 (0.1)	P	98AKa, 75AA, 70HAa
$\text{Pr}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	3.8 (0.2)	P	75AA
	MHL + H	0.1; $\text{KNO}_3$	25	2.4 (0.2)	P	75AA
$\text{Nd}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	3.9 (0.2)	P	75AA, 70HAa, 69YMa
	MHL + H	0.1; $\text{KNO}_3$	25	2.6 (0.2)	P	75AA, 69YMa
	ML + M	0.1; $\text{KNO}_3$	25	3.9 (0.2)	P	70HAa
$\text{Sm}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	4.5 (0.2)	P	75AA, 69LUa
	MHL + H	0.1; $\text{KNO}_3$	25	2.6 (0.2)	P	75AA, 69LUa
$\text{Eu}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	4.7 (0.2)	P	75AA
	MHL + H	0.1; $\text{KNO}_3$	25	3.1 (0.2)	P	75AA
$\text{Gd}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	4.5 (0.2)	P	75AA
	MHL + H	0.1; $\text{KNO}_3$	25	2.4 (0.2)	P	75AA
$\text{Tb}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	4.4 (0.2)	P	75AA
	MHL + H	0.1; $\text{KNO}_3$	25	2.3 (0.2)	P	75AA
$\text{Dy}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	4.5 (0.2)	P	75AA
	MHL + H	0.1; $\text{KNO}_3$	25	2.3 (0.2)	P	75AA
$\text{Ho}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	5.0 (0.2)	P	75AA
	MHL + H	0.1; $\text{KNO}_3$	25	2.3 (0.2)	P	75AA
$\text{Tm}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	4.7 (0.2)	P	75AA
	MHL + H	0.1; $\text{KNO}_3$	25	2.7 (0.2)	P	75AA
$\text{Yb}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	4.8 (0.2)	P	75AA
	MHL + H	0.1; $\text{KNO}_3$	25	2.5 (0.2)	P	75AA
$\text{Lu}^{3+}$	ML + H	0.1; $\text{KNO}_3$	25	5.0 (0.2)	P	75AA
$\text{Th}^{4+}$	ML + H	0.1; $\text{KNO}_3$	25	3.1 (0.2)	P	70HAa
$\text{U}^{4+}$	ML + H	0.1; $\text{KNO}_3$	25	2.3 (0.2)	P	68CMb

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Table 4 (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
$\text{UO}_2^{2+}$	$\text{ML} + \text{H}$	0.1; $\text{KNO}_3$	25	2.3 (0.2)	P	82OLa
	$\text{M} + \text{H}_2\text{L}$	0.1; $\text{KNO}_3$	25	7.6 (0.2)	P	82OLa
	$\text{M} + \text{H}_3\text{L}$	0.1; $\text{KNO}_3$	25	5.5 (0.2)	P	82OLa
	$2\text{M} + \text{H}_2\text{L}$	0.1; $\text{KNO}_3$	25	11.8 (0.2)	P	82OLa

<sup>a</sup>As far as  $\text{Na}^+$  forms complexes with complexones, the use of NaOH instead of KOH for titrations of  $\text{H}_6\text{ttha}$  in solutions with potassium salts as inert electrolytes should be avoided. NaOH leads to pH and  $\lg K(\text{H} + \text{L})$  values for  $\text{Httha}^{5-}$  [82OLa, 71LUa, 65BMf] lower than those obtained with KOH. There are no adequate investigations on  $\text{Na}^+$  interaction, in contrast to the case of EDTA. From the TTHA protonation constants reported, the formation of a  $[\text{Na}(\text{ttha})]^{5-}$ , and probably of a  $[\text{Na}_2(\text{ttha})]^{4-}$ , complex appears possible. This explains why the protonation constants obtained by [65BMf] for  $\text{ttha}^{6-}$  (10.19) and  $\text{Httha}^{5-}$  (9.40) from titration of  $\text{H}_6\text{ttha}$  with NaOH in 0.1 mol  $\text{L}^{-1}$   $\text{KNO}_3$  and 25  $^\circ\text{C}$  are lower than those shown in Table 4, for which KOH was used. In contrast for the same conditions (inert salt concentration and temperature), nearly 40 years later Letkeman et al. using  $\text{KNO}_3$  obtained  $\lg K(\text{H} + \text{L}) = 10.68$  [79LMA]. For this reason, the data presented by [65BMf], as well as those of [71LUa] and [82OLa], were excluded from the evaluation, although these values have been used in the calculation of stability constants by a large number of researchers, particularly those from North Europe [70HAA]. The resultant constants are lower and require correction in order to allow comparison with other values. For  $I = 0.1$  mol  $\text{L}^{-1}$   $\text{KNO}_3$  and 25  $^\circ\text{C}$ , the protonation constants measured by titration with KOH [98AKa, 97DFa, 79LMA, 76HMD] give the accepted values in Table 4.

For  $\text{Na}^+$ , the complex formation has not been studied in detail. The single published value for  $\text{Na}^+$   $\lg K(\text{Na} + \text{L}) = 1.00$  is from a kinetic study of the reaction of the nickel(II)-TTHA complex with cyanide [80KNa]. Here, as also in other cases with TTHA, more studies are needed based on crystalline sodium compounds as was done for EDTA, in order to have information on the sodium coordination. Similar remarks are also valid for the other alkali cations.

<sup>b</sup>For  $\text{Mg}^{2+}$ , the  $\lg K_{\text{ML}}$  value was recalculated by the reviewer; the published value ( $\lg K_{\text{ML}} = 8.43$ ), for which the protonation constants of [65BMf] had been used, was increased by 0.07 to 8.5.

<sup>c</sup>The TTHA complexation of  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  is characterized by formation of ML as well as  $\text{M}_2\text{L}$  complexes. Both are present in mixtures with metal:ligand total molar concentration ratio 1:1. In several papers, this fact was not considered [80KHb, 80MMd], leading to erroneous constants. For  $\text{Al}^{3+}$ , only the values from [98ACa, 70HAA] and for  $\text{Ga}^{3+}$  those from [98ACa, 98AKa, 97DFa] are accepted. Additional values from these references, despite large standard deviations, are considered as the most reliable:  $\lg K(\text{Al} + \text{L}) = 20.0$  (0.3),  $\lg K(2\text{Al} + \text{L}) = 28.8$  (0.3),  $\lg K(\text{Al}_2\text{L} + 2\text{OH}) = 16.8$  (0.9),  $\lg K(\text{GaH}_2\text{L} + \text{L}) = 2.1$  (0.3),  $\lg K(\text{GaL} + \text{Ga}) = 13.8$  (1.4),  $\lg K(\text{Ga}_2\text{L} + 2\text{OH}) = 19.7$  (0.5),  $\lg K(\text{Ga}_2\text{L} + \text{H}) = 1.2$  (0.5) (0.1 mol  $\text{L}^{-1}$   $\text{K/Me}_4\text{NNO}_3$ , 25  $^\circ\text{C}$ ).

<sup>d</sup>For  $\text{In}^{3+}$ , the data presented by [97DFa]  $\lg K(\text{In} + \text{L}) = 26.9$  (0.5) and  $\lg K(\text{InL} + \text{In}) = 9.0$  (0.5) for 0.1 mol  $\text{L}^{-1}$   $\text{KNO}_3$  and 25  $^\circ\text{C}$  are the most reliable, although the uncertainty is greater than for **Provisional** assignment. The value reported in [84TMC] ( $\lg K(\text{In} + \text{L}) = 26.75$ ; 0.1 mol  $\text{L}^{-1}$   $\text{KCl}$ , 25  $^\circ\text{C}$ , Conc., gl) is in close agreement with that in [97DFa], but the description of experimental conditions is inadequate.

<sup>e</sup>For  $\text{Tl}^{3+}$ , the most reliable value is:  $\lg K(\text{Tl} + \text{L}) = 41$  (1), 1.0 mol  $\text{L}^{-1}$   $\text{NaClO}_4$ , 25  $^\circ\text{C}$  [00CLa].

<sup>f</sup>The fair agreement amongst other results for  $\text{Pb}^{2+}$ , allows specification of acceptable values, but some caution is needed in evaluation of their precision:  $\lg K(\text{Pb}_2\text{L} + \text{H}) = 2.6$  (0.4),  $\lg K(\text{Pb}_2\text{HL} + \text{H}) = 2.3$  (0.4) [70HAA, 69LUa] in 0.1 mol  $\text{L}^{-1}$   $\text{KNO}_3$ , 25  $^\circ\text{C}$ .

<sup>g</sup>The determination of equilibrium constants from pH measurements in solutions containing a metal ion and a ligand is normally done avoiding the presence of polymeric hydrolysis products. In this respect, some caution is needed for metal ions such as  $\text{Bi}^{3+}$ , which forms  $\text{Bi}_6(\text{OH})_{12}^{6+}$  below pH 1.5. Apparently, the authors of [69YMa] used data for the determination of the different constants of  $\text{Bi}^{3+}$  without considering this fact. In another paper, by use of spectrophotometric measurements, the formation of  $[\text{Bi}(\text{H}_4\text{ttha})]^+$ ,  $[\text{Bi}(\text{H}_3\text{ttha})]$ ,  $[\text{Bi}(\text{Httha})]^{2-}$ , and  $[\text{Bi}(\text{ttha})]^{3-}$  was identified, but the author was not able to calculate the stability constants correctly as "only six" of the nine TTHA protonation constants were known [79NPa]. The corresponding values are therefore rejected in the present study.

<sup>h</sup>The investigations done by [76NAa] with  $\text{VO}^{2+}$  are inconclusive; the stability constants of the ML and  $\text{M}_2\text{L}$  complexes with this cation were not reported as they "are not easy to calculate because of overlapping equilibria". Also, the protonation constants for  $[\text{VO}(\text{ttha})]^{4-}$  are doubtful, because of the claimed presence of  $\text{M}_2\text{L}$  species in the mixture with total molar ratio metal:ligand of 1:1 [76NAa].

<sup>i</sup>Complex formation equilibria between  $\text{Fe}^{2+}$  and complexones are amongst the most difficult to study. This is because of its tendency to oxidize to the more stable TTHA-complex of trivalent iron. This process strongly influences the formation of the  $\text{Fe}^{2+}$ -complex. Only one paper was published: [65SCb]. The reported results indicate formation of ML,  $\text{M}_2\text{L}$ , and protonated complexes. However, no recommendation is possible. For comparison, see  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$ .

<sup>j</sup>For  $\text{Fe}^{3+}$ , two papers [65SCb, 70HAA] present similar results: for a 1:1 total molar ratio of metal:ligand a protonated complex

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**Table 4** (Continued).

MHL forms with  $\lg K(\text{FeL} + \text{H})$  close to 8. For a 2:1 molar ratio, the complexes  $\text{Fe}_2\text{L}$  and  $\text{Fe}_2(\text{OH})_2\text{L}^{2-}$  form. As for the analogous complex  $\text{Na}_2[\text{Ga}_2(\text{OH})_2\text{ttha}(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$  [98ACc], the latter has two equivalent  $\text{Fe}^{\text{III}}$  cations, each binding five donor atoms of one half of  $\text{ttha}^{6-}$  ion. The remaining coordinated  $\text{H}_2\text{O}$  molecules undergo  $\mu$ -diol formation with loss of one proton in acidic solution. In [70HAa], there is insufficient experimental information and a doubtful conversion of activities into concentrations. The values  $\lg K(\text{Fe} + \text{L}) = 27.3$  (0.5) [97DFa, 70HAa] and  $\lg K(2\text{Fe} + \text{L}) = 40.2$  (0.5) for  $\text{Fe}^{3+}$  in  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ ,  $25^\circ \text{C}$  are therefore treated as approximate.

<sup>k</sup>The assumption that only homobinuclear and not heterobinuclear species are present in solution has no theoretical justification. In [70LAd], the formation of  $[\text{CaCu}(\text{ttha})]^{2-}$  and  $[\text{CaZn}(\text{ttha})]^{2-}$  was reported; further Kopanica [71NK, 73HKb] reported equilibrium constants for the formation of  $[\text{CdNi}(\text{ttha})]^{2-}$ ,  $[\text{ZnNi}(\text{ttha})]^{2-}$ ,  $[\text{ZnCd}(\text{ttha})]^{2-}$  and  $[\text{CuNi}(\text{ttha})]^{2-}$ . More recently the copper(II) and nickel(II) complexes of  $[\text{Th}(\text{ttha})]^{2-}$ ,  $[\text{Fe}(\text{ttha})]^{3-}$  [85MSc], and  $[\text{Tl}(\text{ttha})]^{3-}$  [00CLa] were characterized.

Another important point in relation to [70HAa] is the systematic use of unbuffered (pH or pM) solutions for electrode potential measurements. The error in the calculated constant could be significantly reduced by use of buffered (pM or pH) solutions, as in the determination of  $K(\text{Hg} + \text{L})$  (using solutions with known and similar concentrations of  $\text{HgL}$  and excess of L), and for  $K(2\text{Hg} + \text{L})$  (using solutions with known and similar concentrations of  $\text{HgL}$  and  $\text{Hg}_2\text{L}$ ). Buffering is also important to reduce the effect of any impurities in the inert salt.

<sup>l</sup>For  $\text{Co}^{2+}$ , the values obtained by [70HAa] are more convincing than those of [67BMd], because in solutions with a total concentration molar ratio  $[\text{Cation}]:[\text{Ligand}] = 1:1$  the species  $\text{Co}_2\text{H}_p\text{L}^{(p-2)+}$  are considered in the evaluation of the constants. This is particularly important because, as a consequence of the formation of  $\text{Co}_2\text{H}_p\text{L}^{(p-2)+}$  species, a certain amount of TTHA, not bound by M, is present in solution. Calculations from these experimental data considering uniquely the presence of  $\text{MH}_p\text{L}$  species give erroneous results. The data  $\lg K(\text{Co} + \text{L}) = 18.2$  (0.3) and  $\lg K(\text{CoL} + \text{Co}) = 11.7$  (0.3) in  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ ,  $25^\circ \text{C}$  [70HAa] are the most reliable.

<sup>m</sup>The value published by [69Bhb] for  $\text{Co}^{3+}$  is considered approximate:  $\lg K(\text{M} + \text{L}) = 49.5$  (0.5) in  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ ,  $25^\circ \text{C}$ .

<sup>n</sup>For  $\text{Ni}^{2+}$ , the values of [70HAa]  $\lg K(\text{Ni} + \text{L}) = 19.1$  (0.3) and  $\lg K(\text{NiL} + \text{Ni}) = 14.2$  (0.3),  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ ,  $25^\circ \text{C}$  are outside the precision requirements of the present review.

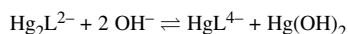
<sup>o</sup>Three papers report values for  $\lg K(\text{Cu} + \text{L})$  in  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$  that are in poor agreement: 19.2 ([70HAa],  $25^\circ \text{C}$ ), 21.87 ([69ALb],  $20^\circ \text{C}$ ) and 20.3 ([67BMd],  $25^\circ \text{C}$ ), but with fair agreement for  $\lg K(\text{CuL} + \text{H})$  [69ALb, 70HAa, 67BMd]: 8.03; 7.96 and 8.0, Table 4. For  $\text{CuL}$ , the mean value  $\lg K(\text{Cu} + \text{L}) = 20.5 \pm 1.3$  has an uncertainty that exceeds our criteria. Unfortunately, the values from [84HKa] presented in [03IU] are the secondary citation from [89MS], and therefore cannot be considered here.

<sup>p</sup>For  $\text{Cd}^{2+}$ , the values presented by [70HAa]:  $\lg K(\text{CdHL} + \text{H}) = 3.2$  (0.3);  $\lg K(\text{CdL} + \text{Cd}) = 8.2$  (0.3) are considered to be the most reliable, although the uncertainties are outside the precision limits assumed for "Provisional" classification.

<sup>q</sup>In the case of  $\text{Hg}^{2+}$ , several authors tried to use a mercury electrode, but had limited success in obtaining equilibrium constants.

In the case of  $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$  as inert salt [66SCb], difficulties are expected in the measurement of potentials between a mercury electrode and the saturated calomel electrode (SCE). This is because of the insolubility of  $\text{KClO}_4$ , which is formed at the contact boundary between the investigated solution and that of the reference electrode ( $3.74 \text{ mol L}^{-1} \text{ KCl}$ ). This problem is avoided by use of  $\text{KNO}_3$  as inert salt [70HAa]. Further, preliminary measurements by [76NAa] using a mercury electrode in solution with  $\text{Hg}^{\text{II}}$ ,  $\text{V}^{\text{IV}}$ , and TTHA in total molar ratio 1:1:1 showed the formation of a precipitate, even at high pH. Schröder [66SCb] noted the formation of a precipitate at a total molar ratio  $[\text{Hg}]:[\text{TTHA}] = 2:1$ , following addition of  $\text{Hg}^{\text{II}}$  to a  $\text{H}_6\text{ttha}$  solution. However, the precipitate dissolved after base addition. For this, he assumed the formation of  $[\text{Hg}_2(\text{OH})_2\text{ttha}]^{4-}$ , but without any experimental confirmation.

<sup>r</sup>The hydrolysis of  $\text{Hg}_2\text{L}$  does not correspond to the formation of  $\text{Hg}_2(\text{OH})_2\text{L}$  [66SCb, 70HAa] but to the following reaction:



with formation of soluble monomolecular  $\text{Hg}(\text{OH})_2$  [90AC, 58ASa].

<sup>s</sup>According to Ermakov and coauthors, the complex formation with  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$  in  $1\text{--}2 \text{ mol L}^{-1} \text{ HClO}_4$  occurs with formation of  $\text{MH}_2\text{ttha}$ :  $\lg K(\text{M} + \text{H}_2\text{L}) = 19.7$  (Zr) and 19.1 (Hf) [66Enc]. As the exact composition of acidic solutions of these cations is still unknown, it is not possible to evaluate the importance of these results. Besides, no cationic TTHA species were considered.

<sup>t</sup>From alkalimetric titrations of protonated TTHA in the presence of disodium molybdate, Lund [71LUa] ( $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ ,  $25^\circ \text{C}$ ) determined the equilibrium constants of eight different complexes:  $\lg K(2\text{MoO}_4 + \text{H}_6\text{L} \rightleftharpoons (\text{MoO}_3)_2\text{H}_2\text{L} + 2\text{H}_2\text{O})$  13.80 (0.25);  $\lg K(2\text{MoO}_4 + \text{H}_5\text{L} \rightleftharpoons (\text{MoO}_3)_2\text{HL} + 2\text{H}_2\text{O})$  11.70 (0.25);  $\lg K(2\text{MoO}_4 + \text{H}_4\text{L} \rightleftharpoons (\text{MoO}_3)_2\text{L} + 2\text{H}_2\text{O})$  8.4 (0.3);  $\lg K(\text{MoO}_4 + \text{H}_6\text{L} \rightleftharpoons \text{MoO}_3\text{H}_4\text{L} + \text{H}_2\text{O})$  7.45 (0.30);  $\lg K(\text{MoO}_4 + \text{H}_5\text{L} \rightleftharpoons \text{MoO}_3\text{H}_3\text{L} + \text{H}_2\text{O})$  6.7 (0.3);  $\lg K(\text{MoO}_4 + \text{H}_4\text{L} \rightleftharpoons \text{MoO}_3\text{H}_2\text{L} + \text{H}_2\text{O})$  5.60 (0.25);  $\lg K(\text{MoO}_4 + \text{H}_3\text{L} \rightleftharpoons \text{MoO}_3\text{HL} + \text{H}_2\text{O})$  3.2 (0.3);  $\lg K(\text{MoO}_4 + \text{H}_2\text{L} \rightleftharpoons \text{MoO}_3\text{L} + \text{H}_2\text{O})$  3.1 (0.3). The protonation constants of TTHA were determined under the same conditions. "The  $(\text{MoO}_3)_2\text{L}^{6-}$  complex was, however, just on the limit of detection, and the stability constant of that complex should consequently be regarded with suspicion", Lund [71LUa]. An examination of the complex distribution diagram shows that similar conclusions are valid also for  $\text{MoO}_3\text{HL}^{5-}$ ,  $\text{MoO}_3\text{H}_3\text{L}^{3-}$ , and  $\text{MoO}_3\text{H}_4\text{L}^{2-}$ . This remark was considered in our assignment of uncertainty.

(continues on next page)

**Table 4** (Continued).

<sup>u</sup>Among the rare earth trivalent cations, the information given in [69HGa] on the Ce<sup>3+</sup> complexes cannot be considered because the temperature and the use of an inert salt are not specified.

The most important studies on trivalent lanthanide complexes are those of [70HAa, 69LUa] and [75AA]. The latter represents a systematic investigation of 12 different cations excluding Er and Pm. These cations have a coordination number larger than six and form very stable ML complexes with TTHA. In [Ln(ttha)]<sup>3-</sup>, few donor atoms remain free for a second cation, thus, the stability constants for formation of [M<sub>2</sub>(ttha)] from [M(ttha)]<sup>3-</sup> are small, their logarithmic values being lower than 4. For lg *K*(M + L), the following approximate values are reported: La<sup>3+</sup>: 23.4 (1) [98AKa, 75AA, 70HAa, 65BMf], Pr<sup>3+</sup>: 23.7 (1) [75AA], Nd<sup>3+</sup>: 23.8 (1) [75AA, 70HAa], Sm<sup>3+</sup>: 23.7 (1) [75AA], Eu<sup>3+</sup>: 23.5 (1) [75AA], Gd<sup>3+</sup>: 23.5 (1) [75AA], Tb<sup>3+</sup>: 23.6 (1) [75AA], Dy<sup>3+</sup>: 23.7 (1) [75AA], Ho<sup>3+</sup>: 23.6 (1) [75AA], Er<sup>3+</sup>: 23.2 (1) [70HAa], Tm<sup>3+</sup>: 23.2 (1) [75AA], Yb<sup>3+</sup>: 23.0 (1) [75AA] and Lu<sup>3+</sup>: 23.0 (1) [75AA].

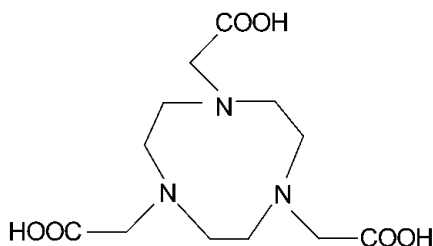
The large standard deviations are a consequence of the difficulty in determining values of lg *K*(M + L) > 20. The s.d. assigned above corresponds to that for a pH shift of only 0.04. Only in the case of Hg<sup>2+</sup>, but by use of a very sensitive and stable electrode, can the s.d. have a lower value.

The values lg *K*(ErL + H) = 4.5 (0.2) and lg *K*(ErL + Er) = 3.8 (0.2) of [70HAa] contrast with those presented in [75AA] for other lanthanide ions.

<sup>v</sup>The value for Th<sup>IV</sup> [70HAa] is accepted as approximate: lg *K*(M + L) = 32 (1) (0.1 mol L<sup>-1</sup> KNO<sub>3</sub>, 25 °C).

<sup>w</sup>The value in [69DBa] for Am<sup>3+</sup> lg *K*(M + L) = 27.6 (0.1 mol L<sup>-1</sup> NH<sub>4</sub>ClO<sub>4</sub>, 25 °C) contrasts with data published for Ln<sup>III</sup> complexes (ca. 4 lg units higher). Further research is therefore needed.

### 9. 2,2',2''-(1,4,7-TRIAZANONANE-1,4,7-TRIYL)TRIACETIC ACID, NOTA, H<sub>3</sub>nota



*Cations studied:* H<sup>+</sup> <sup>a</sup>: 96GEb, 93KT, 91GSa, 91CMd, 87BGc, 85GS, 85MBb

Mg <sup>2+</sup> <sup>b</sup> :	87BGc, 85MBb	Co <sup>2+</sup> :	75HTa	Eu <sup>3+</sup> <sup>e</sup> :	97WHb, 87CN
Ca <sup>2+</sup> <sup>b</sup> :	87BGc, 85MBb	Cu <sup>2+</sup> <sup>d</sup> :	87BGc, 75HTa	Gd <sup>3+</sup> <sup>e</sup> :	91BCa, 90BSe, 87CN
Sr <sup>2+</sup> <sup>b</sup> :	87BGc	Zn <sup>2+</sup> :	75HTa	Tb <sup>3+</sup> <sup>e</sup> :	87CN
Ba <sup>2+</sup> <sup>b</sup> :	87BGc	Cd <sup>2+</sup> :	75HTa	Dy <sup>3+</sup> <sup>e</sup> :	87CN
Ga <sup>3+</sup> :	91CMd	La <sup>3+</sup> <sup>e</sup> :	87CN	Ho <sup>3+</sup> <sup>e</sup> :	87CN
In <sup>3+</sup> :	91CMd	Ce <sup>3+</sup> <sup>e</sup> :	90BSe, 87CN	Er <sup>3+</sup> <sup>e</sup> :	87CN, 90BSe
Pb <sup>2+</sup> :	75HTa	Pr <sup>3+</sup> <sup>e</sup> :	87CN	Tm <sup>3+</sup> <sup>e</sup> :	87CN
Mn <sup>2+</sup> <sup>c</sup> :	90CBc, 75HTa	Nd <sup>3+</sup> <sup>e</sup> :	87CN	Yb <sup>3+</sup> <sup>e</sup> :	87CN
Fe <sup>3+</sup> :	91CMd	Sm <sup>3+</sup> <sup>e</sup> :	87CN	Lu <sup>3+</sup> <sup>e</sup> :	87CN

*Experimental conditions of papers selected for critical evaluation:*

- I* = 0.1 mol L<sup>-1</sup> NaNO<sub>3</sub>, 25 °C, Conc., gl: 87BGc
- I* = 0.1 mol L<sup>-1</sup> NaNO<sub>3</sub>, 35 °C, Conc., gl: 87BGc
- I* = 0.1 mol L<sup>-1</sup> KNO<sub>3</sub>, 25 °C, Conc., gl: 96GEb
- I* = 0.1 mol L<sup>-1</sup> KCl, 25 °C, Conc., gl: 91CMd
- I* = 0.1 mol L<sup>-1</sup> KCl, 25 °C, Conc., sp: 91CMd
- I* = 0.1 mol L<sup>-1</sup> (CH<sub>3</sub>)<sub>4</sub>NCl, 25 °C, Conc., gl: 91CMd
- I* = 1.0 mol L<sup>-1</sup> NaClO<sub>4</sub>, 25 °C, Conc., gl: 87BGc
- I* = 1.0 mol L<sup>-1</sup> NaClO<sub>4</sub>, 35 °C, Conc., gl: 87BGc

$I = 1.0 \text{ mol L}^{-1} \text{ NaClO}_4$ , 25 °C, Conc., sp: 87BGc

$I = 0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ , 35 °C, Conc., sp: 87BGc

**Table 5** Recommended and provisional data for NOTA<sup>f</sup>.

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
$\text{H}^+$ <sup>a</sup>	H + L	0.1; $\text{NaNO}_3$	25	11.73 (0.02)	P	87BGc
		0.1; $\text{NaNO}_3$	35	11.58 (0.02)	P	87BGc
		0.1; $\text{K}/(\text{CH}_3)_4\text{NCl}$	25	11.98 (0.03)	P	91CMd
		1.0; $\text{NaClO}_4$	25	10.77 (0.01)	P	87BGc
		1.0; $\text{NaClO}_4$	35	10.54 (0.01)	P	87BGc
	HL + H	0.1; $\text{NaNO}_3$	25	5.74 (0.01)	R1	87BGc
		0.1; $\text{NaNO}_3$	35	5.67 (0.01)	R1	87BGc
		0.1; $\text{K}/(\text{CH}_3)_4\text{NCl}$	25	5.65 (0.02)	R1	91CMd
		0.1; $\text{NaClO}_4$	25	5.62 (0.04)	R1	96GEb
		0.1; $\text{KNO}_3$	25	5.58 (0.04)	R1	96GEb
		1.0; $\text{NaClO}_4$	25	6.03 (0.01)	R1	87BGc
		1.0; $\text{NaClO}_4$	35	5.93 (0.01)	R1	87BGc
	$\text{H}_2\text{L} + \text{H}$	0.1; $\text{NaNO}_3$	25	3.16 (0.01)	R1	87BGc
		0.1; $\text{NaNO}_3$	35	3.17 (0.01)	R1	87BGc
		0.1; $\text{K}/(\text{CH}_3)_4\text{NCl}$	25	3.18 (0.03)	R1	91CMd
		0.1; $\text{NaClO}_4$	25	3.03 (0.04)	R1	96GEb
		0.1; $\text{KNO}_3$	25	2.97 (0.04)	R1	96GEb
		1.0; $\text{NaClO}_4$	25	3.16 (0.01)	R1	87BGc
		1.0; $\text{NaClO}_4$	35	3.19 (0.01)	R1	87BGc
	$\text{H}_3\text{L} + \text{H}$	1.0; $\text{NaClO}_4$	25	1.96 (0.01)	P	87BGc
		1.0; $\text{NaClO}_4$	35	2.02 (0.01)	P	87BGc
$\text{Mg}^{2+}$ <sup>b</sup>	M + L	0.1; $\text{NaNO}_3$	25	9.69 (0.03)	P	87BGc
		0.1; $\text{NaNO}_3$	35	9.66 (0.03)	P	87BGc
	ML + H	0.1; $\text{NaNO}_3$	25	4.6 (0.2)	P	87BGc
$\text{Ca}^{2+}$ <sup>b</sup>	M + L	0.1; $\text{NaNO}_3$	25	8.92 (0.01)	P	87BGc
		0.1; $\text{NaNO}_3$	35	8.74 (0.01)	P	87BGc
	ML + H	0.1; $\text{NaNO}_3$	25	5.06 (0.03)	P	87BGc
		0.1; $\text{NaNO}_3$	35	5.17 (0.05)	P	87BGc
$\text{Sr}^{2+}$ <sup>b</sup>	M + L	0.1; $\text{NaNO}_3$	25	6.83 (0.01)	P	87BGc
		0.1; $\text{NaNO}_3$	35	6.76 (0.01)	P	87BGc
	ML + H	0.1; $\text{NaNO}_3$	25	6.30 (0.01)	P	87BGc
		0.1; $\text{NaNO}_3$	35	6.00 (0.01)	P	87BGc
$\text{Ba}^{2+}$ <sup>b</sup>	M + L	0.1; $\text{NaNO}_3$	25	5.10 (0.01)	P	87BGc
		0.1; $\text{NaNO}_3$	35	5.06 (0.01)	P	87BGc
$\text{Ga}^{3+}$	M + L	0.1; $\text{KCl}$	25	31.0 (0.2)	P	91CMd
	ML + OH	0.1; $\text{KCl}$	25	4.1 (0.1)	P	91CMd
$\text{In}^{3+}$	M + L	0.1; $\text{KCl}$	25	26.2 (0.2)	P	91CMd
	ML + OH	0.1; $\text{KCl}$	25	7.2 (0.1)	P	91CMd
$\text{Fe}^{3+}$	M + L	0.1; $\text{KCl}$	25	28.3 (0.1)	P	91CMd

(continues on next page)



Table 5 (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$t/^\circ\text{C}$	$\lg K$	Category	References
$\text{Cu}^{2+ \text{ d}}$	M + L	1.0; $\text{NaClO}_4$	25	21.63 (0.03)	P	87BGc
		1.0; $\text{NaClO}_4$	35	21.30 (0.03)	P	87BGc
	ML + H	1.0; $\text{NaClO}_4$	25	2.74 (0.06)	P	87BGc
		1.0; $\text{NaClO}_4$	35	2.74 (0.06)	P	87BGc

<sup>a</sup>Enthalpy and entropy changes for protonation reactions have been derived from the temperature dependence of the protonation constants in the range 15–55 °C [87BGc]: for H + L,  $\Delta_r H_c = -46$  (7)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 68$  (22)  $\text{J K}^{-1} \text{ mol}^{-1}$  (0.1  $\text{mol L}^{-1}$   $\text{NaNO}_3$ );  $\Delta_r H_c = -46$ (4)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 52$  (12)  $\text{J K}^{-1} \text{ mol}^{-1}$  (1  $\text{mol L}^{-1}$   $\text{NaClO}_4$ ); for HL + H,  $\Delta_r H_c = -8.8$  (0.8)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 80$  (3)  $\text{J K}^{-1} \text{ mol}^{-1}$  (0.1  $\text{mol L}^{-1}$   $\text{NaNO}_3$ );  $\Delta_r H_c = -16.3$  (0.4)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 61$  (2)  $\text{J K}^{-1} \text{ mol}^{-1}$  (1  $\text{mol L}^{-1}$   $\text{NaClO}_4$ ); for  $\text{H}_2\text{L} + \text{H}$ ,  $\Delta_r H_c = 5.9$  (0.8)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 80$  (3)  $\text{J K}^{-1} \text{ mol}^{-1}$  (0.1  $\text{mol L}^{-1}$   $\text{NaNO}_3$ );  $\Delta_r H_c = 5.4$  (0.4)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 78$  (1)  $\text{J K}^{-1} \text{ mol}^{-1}$  (1  $\text{mol L}^{-1}$   $\text{NaClO}_4$ ); for  $\text{H}_3\text{L} + \text{H}$ ,  $\Delta_r H_c = 5$  (3)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 54$  (9)  $\text{J K}^{-1} \text{ mol}^{-1}$  (1  $\text{mol L}^{-1}$   $\text{NaClO}_4$ ).

<sup>b</sup>Enthalpy and entropy changes for complexation have been derived from the temperature dependence of the ML stability constants in the range 15–55 °C, or 25–55 °C, [87BGc]. For  $\text{Mg}^{2+}$  (where no value was determined at 15 °C because of the long equilibration time):  $\Delta_r H_c = 2$  (4)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 188$  (13)  $\text{J K}^{-1} \text{ mol}^{-1}$ ; for  $\text{Ca}^{2+}$ ,  $\Delta_r H_c = -25$  (1)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 88$  (4)  $\text{J K}^{-1} \text{ mol}^{-1}$ ; for  $\text{Sr}^{2+}$ ,  $\Delta_r H_c = -9$  (1)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 100$  (4)  $\text{J K}^{-1} \text{ mol}^{-1}$ ; for  $\text{Ba}^{2+}$ ,  $\Delta_r H_c = -5.8$  (0.5)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 78$  (2)  $\text{J K}^{-1} \text{ mol}^{-1}$ .

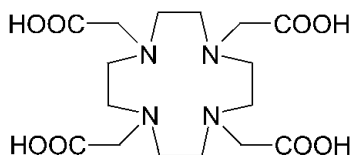
<sup>c</sup>For  $\text{Mn}^{2+}$ , an average value of  $\lg K_{\text{ML}} = 14.6$  (0.3) ( $I = 0.1 \text{ mol L}^{-1}$   $\text{Me}_4\text{NCl}$ , 25 °C, relaxation rate measurements, Conc. [90CBc], and  $I = 0.1 \text{ mol L}^{-1}$   $\text{KNO}_3$ , 25 °C, polarography, Conc. [75HTa]) is considered to be reliable.

<sup>d</sup>Enthalpy and entropy of complexation have been derived from the temperature dependence of the stability constants in the range 15–55 °C [87BGc]: for Cu + L,  $\Delta_r H_c = -56$  (3)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = 226$  (8)  $\text{J K}^{-1} \text{ mol}^{-1}$ ; for  $\text{CuL} + \text{H}$ ,  $\Delta_r H_c = 0.4$  (3)  $\text{kJ mol}^{-1}$  and  $\Delta_r S_c = -54$  (8)  $\text{J K}^{-1} \text{ mol}^{-1}$ .

<sup>e</sup>Two publications [97WHb, 87CN] report stability constants for lanthanides. [97WHb] gives  $\lg K(\text{M} + \text{L}) = 13.9$  (0.1) for  $\text{Eu}^{3+}$  from a luminescence-based method, whereas [87CN] gives values for the full series of cations, but only as a graphical representation of the values obtained from competitive spectrophotometric measurements using arsenazo(III) as auxiliary ligand.

<sup>f</sup>The quality of data presented by [87BGc] is generally high. If there had been at least one  $\lg K_{\text{ML}}$  value from an independent group to give R-level with [87BGc], then all of the values in Table 5 represented by [87BGc] could have been nominated as **R1**. No such result is available.

## 10. 2,2',2'', 2'''-(1,4,7,10-TETRAAZACYCLODODECANE -1,4,7,10-TETRAYL) TETRAACETIC ACID, DOTA, $\text{H}_4\text{dota}$



*Cations studied:*  $\text{H}^+$  <sup>a,b</sup>: 00BCa, 98BFa, 96CHc, 95KKa, 95PMa, 94KCa, 94TBb, 93KCa, 92CDd, 91DSa, 91CMA, 84DFa, 82DSa, 81DMA, 81SFa, 79DE, 76SFb

$\text{Li}^+$ <sup>c</sup> :	82DSa	$\text{Sr}^{2+}$ :	96CHc, 91CMA, 84DFa,	$\text{Co}^{2+}$ <sup>e</sup> :	92CDd, 91CMA,
$\text{Na}^+$ :	00BCa, 82DSa,		82DSa, 81SFa, 76SFb		84DFa, 82DSa, 81SFa,
	81DMA, 79DE	$\text{Ba}^{2+}$ :	96CHc, 91CMA, 84DFa,		76SFb
$\text{K}^+$ :	91CMA, 82DSa		82DSa, 81SFa, 76SFb	$\text{Ni}^{2+}$ <sup>e</sup> :	91CMA, 84DFa, 82DSa,
$\text{Be}^{2+}$ <sup>d</sup> :	82DSa	$\text{Al}^{3+}$ :	95KKa		81SFa, 76SFb
$\text{Mg}^{2+}$ :	96CHc, 91CMA, 84DFa,	$\text{Ga}^{3+}$ :	91CMB	$\text{Cu}^{2+}$ <sup>e</sup> :	00BCa, 92CDd,
	82DSa, 81SFa, 76SFb	$\text{In}^{3+}$ :	91CMB		91CMA, 84DFa,
$\text{Ca}^{2+}$ :	00BCa, 96CHc,	$\text{Mn}^{2+}$ :	01BCa, 92CDd, 81SFa		82DSa, 81SFa, 76SFb
	91CMA, 84DFa,	$\text{Fe}^{2+}$ <sup>e</sup> :	92CDd		
	82DSa, 81SFa, 76SFb	$\text{Fe}^{3+}$ :	91CMB		

<b>Zn<sup>2+</sup>:</b>	00BCa, 92CDd, 91Cma, 84DFa, 82DSa, 81SFa, 76SFb	<b>Pr<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN	<b>Tb<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN, 86LDd
<b>Cd<sup>2+</sup>:</b>	92CDd, 90CCa, 76SFb	<b>Nd<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN	<b>Dy<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN
<b>Hg<sup>2+</sup>:</b>	94KOb	<b>Sm<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN	<b>Ho<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN
<b>Pb<sup>2+</sup> f:</b>	95PMa, 92CDd, 90CCa, 81SFa, 76SFb	<b>Eu<sup>3+</sup>:</b>	97WHb, 95WH, 94TBb, 87CN, 86LDd	<b>Er<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN
<b>Y<sup>3+</sup> g:</b>	94KCa, 91BCc, 89CJ	<b>Gd<sup>3+</sup> h:</b>	00BCa, 97WHb, 96PW, 96BCd, 95WH, 94TBb, 94KCa,	<b>Tm<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN
<b>La<sup>3+</sup> h:</b>	97WH, 94TBb, 91Cmb, 87CN		93KCa, 92AAb, 92WJa, 91Ca,	<b>Yb<sup>3+</sup> h:</b>	98BFa, 97WHb, 94TBb, 87CN
<b>Ce<sup>3+</sup> h:</b>	98BFa, 97WHa, 94TBb, 87CN		91Cmb, 87CN, 79DE	<b>Lu<sup>3+</sup>:</b>	97WHb, 94TBb, 87CN, 86LDd

*Experimental conditions of papers selected for critical evaluation:*

$I = 0.1 \text{ mol L}^{-1} (\text{CH}_3)_4\text{NNO}_3$ , 25 °C, Conc., gl: 92CDd, 91BCc, 82DSa

$I = 0.1 \text{ mol L}^{-1} (\text{CH}_3)_4\text{NCl}$ , 25 °C, Conc., gl: 01BCa, 00BCa, 98BFa, 96BCd, 96CHc, 95PMa, 94KCa

$I = 0.1 \text{ mol L}^{-1} (\text{CH}_3)_4\text{NCl}$ , 25 °C, Conc., sp: 94KCa

$I = 0.1 \text{ mol L}^{-1} \text{KNO}_3$ , 25 °C, Conc., gl: 82DSa

$I = 0.1 \text{ mol L}^{-1} \text{KCl}$ , 25 °C, Conc., gl: 94KCa

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

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$\lg K$	Category	References
H <sup>+</sup> a,b	L + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	11.9 (0.2)	P	00BCa, 94KCa, 95PMa, 92CDd, 82DSa
	HL + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	9.72 (0.03)	R	00BCa, 94KCa, 95PMa, 92CDd, 82DSa
	H <sub>2</sub> L + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	4.60 (0.05)	R	00BCa, 96CHc, 94KCa, 95PMa, 92CDd, 82DSa
		0.1; KNO <sub>3</sub> /Cl	4.5 (0.1)	P	94KCa, 82DSa
	H <sub>3</sub> L + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	4.13 (0.03)	R	00BCa, 98BFa, 94KCa, 95PMa, 92CDd, 82DSa
		0.1; KNO <sub>3</sub> /Cl	4.3 (0.1)	P	94KCa, 82DSa
H <sub>4</sub> L + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NCl	2.36 (0.05)	R	00BCa, 98BFa, 95PMa	
Na <sup>+</sup>	M + L	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	4.2 (0.2)	P	00BCa, 82DSa
K <sup>+</sup>	M + L	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub>	1.6 (0.1)	R1	82DSa
Mg <sup>2+</sup>	M + L	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	11.85 (0.09)	R	96CHc, 82DSa
Ca <sup>2+</sup>	M + L	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	17.2 (0.1)	R	00BCa, 82DSa
	ML + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	3.7 (0.1)	P	00BCa, 82DSa
Sr <sup>2+</sup>	M + L	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	15.0 (0.2)	P	96CHc, 82DSa
Ba <sup>2+</sup>	M + L	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub>	12.9 (0.1)	R1	82DSa
Mn <sup>2+</sup> e	M + L	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	20.0 (0.2)	P	01BCa, 92CDd
	ML + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub> /Cl	4.21 (0.06)	R	01BCa, 92CDd
Co <sup>2+</sup> e	M + L	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub>	20.2 (0.1)	R1	92CDd, 82DSa
	ML + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub>	4.04 (0.05)	R1	92CDd, 82DSa
	MHL + H	0.1; (CH <sub>3</sub> ) <sub>4</sub> NNO <sub>3</sub>	3.5 (0.1)	P	92CDd, 82DSa

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Table 6 (Continued).

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$\lg K$	Category	References
$\text{Ni}^{2+ \text{ e}}$	M + L	0.1; $(\text{CH}_3)_4\text{NNO}_3$	20.0 (0.1)	R1	82DSa
$\text{Cu}^{2+ \text{ e}}$	M + L	0.1; $(\text{CH}_3)_4\text{NNO}_3/\text{Cl}$	22.3 (0.1)	R	00BCa, 92CDd, 82DSa
	ML + H	0.1; $(\text{CH}_3)_4\text{NNO}_3/\text{Cl}$	4.30 (0.09)	R	00BCa, 82DSa
	MHL + H	0.1; $(\text{CH}_3)_4\text{NNO}_3/\text{Cl}$	3.55 (0.09)	R	00BCa, 92CDd, 82DSa
$\text{Zn}^{2+ \text{ e}}$	M + L	0.1; $(\text{CH}_3)_4\text{NNO}_3/\text{Cl}$	20.8 (0.2)	P	00BCa, 82DSa
	ML + H	0.1; $(\text{CH}_3)_4\text{NNO}_3/\text{Cl}$	4.24 (0.08)	R	00BCa, 92CDd, 82DSa
	MHL + H	0.1; $(\text{CH}_3)_4\text{NNO}_3/\text{Cl}$	3.51 (0.04)	R	00BCa, 92CDd, 82DSa
$\text{Cd}^{2+}$	M + L	0.1; $(\text{CH}_3)_4\text{NNO}_3$	21.3 (0.1)	R1	92CDd
	ML + H	0.1; $(\text{CH}_3)_4\text{NNO}_3$	4.39 (0.04)	R1	92CDd
	MHL + H	0.1; $(\text{CH}_3)_4\text{NNO}_3$	3.03 (0.05)	R1	92CDd

<sup>a</sup>The first two protonation constant values selected for DOTA were determined in  $(\text{CH}_3)_4\text{NCl}$  or  $(\text{CH}_3)_4\text{NNO}_3$  as supporting electrolyte. Indeed, this ligand forms stable complexes with  $\text{Na}^+$  and also with  $\text{K}^+$ , and media containing these cations lead to lower  $K(\text{H} + \text{L})$  and  $K(\text{HL} + \text{H})$  values.

Another problem is the high value for the first protonation constant of this ligand, which is difficult to determine by the usual potentiometric methods. NMR titration is the preferred technique in such cases but the determined values have not the required precision, because it is difficult: (i) to control the ionic strength; (ii) to prevent reaction with  $\text{CO}_2$  at high pH values through the contact with the atmosphere, and (iii) to convert the constant determined in  $\text{D}_2\text{O}$  to that in  $\text{H}_2\text{O}$ ; see [91DSa]. No other spectroscopic technique is reported.

The protonation constants were also determined in five different mixtures of  $\text{DMSO}/\text{H}_2\text{O}$  (from volume fraction 10 to 50 %), at 25 °C and in 0.1 mol  $\text{L}^{-1}$  in  $(\text{CH}_3)_4\text{NNO}_3$ . The values extrapolated for 100 % of  $\text{H}_2\text{O}$  were identical to those obtained by the same authors by potentiometry in 0.1 mol  $\text{L}^{-1}$   $(\text{CH}_3)_4\text{NNO}_3$  [92CDd].

Reported values range from  $\lg K(\text{L} + \text{H}) = 9.37$  (determined in 0.1 mol  $\text{L}^{-1}$   $\text{NaCl}$  [94KCa]) to 12.6 (in 0.1 mol  $\text{L}^{-1}$   $(\text{CH}_3)_4\text{NCl}$  [98BFa]). Thus, only a provisional assignment is possible.

<sup>b</sup>The values of stability constants determined for metal complexes of DOTA are highly dependent on the values used for  $K(\text{L} + \text{H})$  and  $K(\text{HL} + \text{H})$ . The spread of values found in the literature for the stability constants of metal complexes of DOTA is mainly because of the large range of  $K(\text{L} + \text{H})$  values used by different authors. Those using  $\text{Na}^+$  as supporting electrolyte always obtained the lower values. The same occurs in  $\text{K}^+$  medium, but as the stability constant of the  $\text{K}^+$ -DOTA complex is much smaller, other experimental errors are usually more significant in determining the final value.

<sup>c</sup>The single communication for  $\text{Li}^+$ ,  $\lg K_{\text{LiL}} = 4.3$  (25 °C, 0.1 mol  $\text{L}^{-1}$   $(\text{CH}_3)_4\text{NNO}_3$  [82DSa]) is considered reliable, but needs further independent verification.

<sup>d</sup>DOTA demonstrates a high affinity toward  $\text{Be}^{2+}$  [82DSa], although its selectivity within  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Be}^{2+}$  is not as high as that for TETA. The value  $\lg K_{\text{BeL}} = 13.6$  (25 °C, 0.1 mol  $\text{L}^{-1}$   $(\text{CH}_3)_4\text{NNO}_3$ ) is considered reliable, but for critical evaluation an independent measurement is required.

<sup>e</sup>The macrocyclic framework is folded because of the small size of the cavity. The metal center is coordinated by the four nitrogen atoms and only by two carboxylate groups of the ligand. As the size of the metal ions is not a critical parameter in such structures, the ligand is quite unselective.

<sup>f</sup>The stability constant for  $\text{Pb}^{2+}$  is very high and is difficult to determine by direct potentiometry. Among the values found in the literature, two can be mentioned: one from direct potentiometry,  $\lg K_{\text{PbL}} = 22.69$  (0.03) [90CCa, 92CDd], and the other from spectrophotometry using competition with EDTA ( $\lg K_{\text{PbL}} = 24.3$  (0.2) [95PMa]). The first value can not be accurate because it is too high to be determined by a direct potentiometric measurement, while the second is presented with a very high standard deviation. Without other values, it is impossible to recommend one.

<sup>g</sup>For  $\text{Y}^{3+}$ , an average value of 24.6 (0.3) for  $\lg K_{\text{YL}}$  is considered reliable ( $I = 0.1$  mol  $\text{L}^{-1}$   $(\text{CH}_3)_4\text{NNO}_3$  or  $(\text{CH}_3)_4\text{NCl}$ , 25 °C [94KCa, 91BCc, 89CJ]). The first two publications are based on potentiometric methods and the last one on competition with Arsenazo III followed by spectrophotometric methods.

<sup>h</sup>Several research groups have determined stability constants for the lanthanide-DOTA complexes, but the spread of values is significant. However, for some of the lanthanides, an indicative value is possible:

- $\lg K_{\text{ML}} = 25.0$  (0.3) for  $\text{Ce}^{3+}$  ( $I = 0.1$  mol  $\text{L}^{-1}$   $\text{KCl}$ , 25 °C, luminescence, competition with EDTA [97WHb] and  $I = 0.1$  mol  $\text{L}^{-1}$   $\text{Me}_4\text{NCl}$ , 25 °C, gl, out-of-cell [98BFa]);
- $\lg K_{\text{ML}} = 25.0$  (0.5) for  $\text{Gd}^{3+}$  ( $I = 0.1$  mol  $\text{L}^{-1}$ , 25 °C, gl [91CA],  $I = 0.1$  mol  $\text{L}^{-1}$   $\text{Me}_4\text{NNO}_3$ , 25 °C, fluorescence [93KCa],  $I = 0.1$  mol  $\text{L}^{-1}$   $\text{Me}_4\text{NCl}$ , 25 °C, competition with Arsenazo III, sp [94KCa],  $I = 0.1$  mol  $\text{L}^{-1}$   $\text{Me}_4\text{NCl}$ , 25 °C, competition with EDTA, gl [96BCd, 00BCa]);

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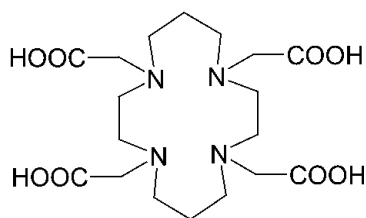
**Table 6** (Continued).

- $\lg K_{ML} = 26.1$  (0.3) for  $\text{Yb}^{3+}$  ( $I = 0.1 \text{ mol L}^{-1}$  KCl, 25 °C, luminescence, competition with EDTA [97WHb],  $I = 0.1 \text{ mol L}^{-1}$   $\text{Me}_4\text{NCl}$ , 25 °C, gl, out-of-cell [98BFa]).

<sup>i</sup>Enthalpy and entropy changes for the protonation reactions of DOTA have been given in two publications [84DFa] and [00BCa], however, there are significant discrepancies between the reported values.

Enthalpy and entropy changes for the complexation reactions of DOTA with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and earth-alkaline metals ( $\text{Ca}^{2+} - \text{Ba}^{2+}$ ) [84DFa], with  $\text{Hg}^{2+}$  [94KOb], and with  $\text{Gd}^{3+}$  [96BCd] have only been determined by one group.

### 11. 2,2',2'', 2'''-(1,4,8,11-TETRAAZACYCLOTETRADECANE-1,4,8,11-TETRAYL) TETRAACETIC ACID, TETA, $\text{H}_4$ teta



*Cations studied:*  $\text{H}^+$  <sup>a</sup>: 92CDd, 91KKa, 91CMA, 84DFa, 82DSa, 81DMA, 81SFa, 76SFb

$\text{Na}^+$ :	82DSa, 81DMA	$\text{Fe}^{2+}$ :	92CDd, 81SFa	$\text{Y}^{3+}$ :	91KKa, 91BCc, 89CJ
$\text{Be}^{2+}$ <sup>b</sup> :	82DSa	$\text{Fe}^{3+}$ <sup>e</sup> :	91CMB	$\text{La}^{3+}$ <sup>f</sup> :	91KKa, 91CMB
$\text{Mg}^{2+}$ :	91CMA, 82DSa, 81SFa, 76SFb	$\text{Co}^{2+}$ :	92CDd, 91CMA, 84DFa, 82DSa, 81SFa, 76SFb	$\text{Ce}^{3+}$ <sup>f</sup> :	91KKa
$\text{Ca}^{2+}$ :	91CMA, 84DFa, 82DSa, 81SFa, 76SFb	$\text{Ni}^{2+}$ :	92CDd, 91CMA, 84DFa, 82DSa, 81SFa, 76SFb	$\text{Nd}^{3+}$ <sup>f</sup> :	91KKa, 86LDb
$\text{Sr}^{2+}$ :	91KKa, 91CMA, 84DFa, 82DSa, 81SFa, 76SFb	$\text{Cu}^{2+}$ :	92CDd, 91CMA, 84DFa, 82DSa, 81SFa, 76SFb	$\text{Sm}^{3+}$ <sup>f</sup> :	91KKa, 86LDb
$\text{Ba}^{2+}$ :	91CMA, 84DFa, 82DSa, 81SFa, 76SFb	$\text{Zn}^{2+}$ <sup>c</sup> :	92CDd, 91CMA, 84DFa, 82DSa, 81SFa, 76SFb	$\text{Eu}^{3+}$ <sup>f</sup> :	97WHb, 91KKa, 86LDb
$\text{Al}^{3+}$ :	95KKa	$\text{Cd}^{2+}$ :	92CDd, 81SFa, 76SFb	$\text{Gd}^{3+}$ <sup>f</sup> :	91KKa, 91CMB, 86LDb
$\text{Ga}^{3+}$ <sup>d</sup> :	91CMB	$\text{Hg}^{2+}$ :	94KOb, 91KKa	$\text{Tb}^{3+}$ <sup>f</sup> :	91KKa
$\text{In}^{3+}$ <sup>d</sup> :	91CMB	$\text{Ag}^+$ :	90KMc	$\text{Dy}^{3+}$ <sup>f</sup> :	86LDb
$\text{Pb}^{2+}$ :	92CDd, 91KKa, 81SFa, 76SFb			$\text{Ho}^{3+}$ <sup>f</sup> :	91KKa
$\text{Mn}^{2+}$ :	92CDd, 81SFa			$\text{Er}^{3+}$ <sup>f</sup> :	86LDb
				$\text{Tm}^{3+}$ <sup>f</sup> :	91KKa
				$\text{Yb}^{3+}$ <sup>f</sup> :	86LDb
				$\text{Lu}^{3+}$ <sup>f</sup> :	91KKa

*Experimental conditions of papers selected for critical evaluation:*

$I = 0.1 \text{ mol L}^{-1}$   $\text{KNO}_3$ , 25 °C, Conc., gl: 92CDd, 82DSa

$I = 0.1 \text{ mol L}^{-1}$  KCl, 25 °C, Conc., gl: 91CMA, 91CMB

$I = 0.1 \text{ mol L}^{-1}$   $(\text{CH}_3)_4\text{NCl}$ , 25 °C, Conc., gl: 91CMA, 91CMB

$I = 1.0 \text{ mol L}^{-1}$  KCl, 25 °C, Conc., luminescence: 97WHb

$I = 0.2 \text{ mol L}^{-1}$   $\text{NaNO}_3$ , 25 °C, Conc., gl: 91KKa; pol: 94KOb

**Table 7** Recommended and provisional data for TETA, 25 °C.

Cation	Equilibrium	$I/\text{mol L}^{-1}$	$\lg K$	Category	References
$\text{H}^+$ <sup>a</sup>	L + H	0.1; $\text{K}/(\text{CH}_3)_4\text{NCl}$	10.7 (0.2)	P	92CDd, 91CMa, 82DSa
	HL + H	0.1; $\text{K}/(\text{CH}_3)_4\text{NCl}$	10.13 (0.03)	R	92CDd, 91CMa, 82DSa
	$\text{H}_2\text{L} + \text{H}$	0.1; $\text{K}/(\text{CH}_3)_4\text{NCl}$	4.10 (0.03)	R	92CDd, 91CMa, 82DSa
	$\text{H}_3\text{L} + \text{H}$	0.1; $\text{K}/(\text{CH}_3)_4\text{NCl}$	3.27 (0.08)	P	92CDd, 91CMa, 82DSa
$\text{Ca}^{2+}$	M + L	0.1; $\text{KNO}_3/\text{Cl}$	8.4 (0.1)	R	91CMa, 82DSa
	ML + H	0.1; $\text{KNO}_3/\text{Cl}$	7.2 (0.2)	P	91CMa, 82DSa
$\text{Sr}^{2+}$	M + L	0.1; $\text{KNO}_3/\text{Cl}$	5.82 (0.09)	R	91CMa, 82DSa
$\text{Ba}^{2+}$	M + L	0.1; $\text{KNO}_3/\text{Cl}$	4.1 (0.2)	P	91CMa, 82DSa
$\text{Mn}^{2+}$	M + L	0.1; $\text{KNO}_3$	11.3 (0.1)	R1	92CDd
$\text{Fe}^{2+}$	M + L	0.1; $\text{KNO}_3$	13.1 (0.1)	R1	92CDd
$\text{Co}^{2+}$	M + L	0.1; $\text{KNO}_3/\text{Cl}$	16.6 (0.1)	R	91CMa, 82DSa
	ML + H	0.1; $\text{KNO}_3/\text{Cl}$	4.2 (0.2)	P	92CDd, 91CMa, 82DSa
	MHL + H	0.1; $\text{KNO}_3/\text{Cl}$	2.84 (0.07)	R1	92CDd, 82DSa
$\text{Ni}^{2+}$	M + L	0.1; $\text{KNO}_3/\text{Cl}$	19.91 (0.07)	R	92CDd, 91CMa, 82DSa
	ML + H	0.1; $\text{KNO}_3/\text{Cl}$	4.2 (0.1)	R	92CDd, 91CMa, 82DSa
	MHL + H	0.1; $\text{KNO}_3/\text{Cl}$	3.2 (0.1)	R	92CDd, 91CMa, 82DSa
$\text{Cu}^{2+}$	M + L	0.1; $\text{KNO}_3/\text{Cl}$	21.7 (0.1)	P	91CMa, 82DSa
	ML + H	0.1; $\text{KNO}_3/\text{Cl}$	3.79 (0.09)	R	92CDd, 91CMa, 82DSa
	MHL + H	0.1; $\text{KNO}_3/\text{Cl}$	2.7 (0.2)	P	91CMa, 82DSa
$\text{Zn}^{2+}$ <sup>c</sup>	ML + H	0.1; $\text{KNO}_3/\text{Cl}$	4.21 (0.08)	R	92CDd, 91CMa, 82DSa
$\text{Cd}^{2+}$	M + L	0.1; $\text{KNO}_3$	18.0 (0.1)	R1	92CDd
	ML + H	0.1; $\text{KNO}_3$	4.04 (0.01)	R1	92CDd
	MHL + H	0.1; $\text{KNO}_3$	2.93 (0.03)	R1	92CDd
$\text{Hg}^{2+}$	M + L	0.2 $\text{NaNO}_3$	25.7 (0.2)	P	94KOb, 91KKa
$\text{Pb}^{2+}$	M + L	0.1; $\text{KNO}_3$	14.3 (0.1)	R1	92CDd
	ML + H	0.1; $\text{KNO}_3$	4.75 (0.02)	R1	92CDd
	MHL + H	0.1; $\text{KNO}_3$	4.25 (0.03)	R1	92CDd
$\text{La}^{3+}$ <sup>f</sup>	M + L	0.1; $\text{KCl}$	11.6 (0.1)	R1	91CMb
	ML + H	0.1; $\text{KCl}$	6.05 (0.01)	R1	91CMb
$\text{Eu}^{3+}$ <sup>f</sup>	M + L	0.1; $\text{KCl}$	14.0 (0.1)	R1	97WHb
$\text{Gd}^{3+}$ <sup>f</sup>	M + L	0.1; $\text{KCl}$	13.8 (0.1)	R1	91CMb
	ML + H	0.1; $\text{KCl}$	4.52 (0.05)	R1	91CMb

<sup>a</sup>Values of protonation constants ( $\lg K$ ) given at other temperatures and ionic strengths are accepted as provisional: (i) H + L 10.11 (0.06), HL + H 9.50 (0.02),  $\text{H}_2\text{L} + \text{H}$  4.02 (0.02),  $\text{H}_3\text{L} + \text{H}$  3.29 (0.04),  $\text{H}_4\text{L} + \text{L}$  1.90 (0.15) ([81DMa],  $I = 1 \text{ mol L}^{-1} \text{ NaCl}$ , 80 °C,  $^1\text{H NMR}$  in  $\text{D}_2\text{O}$ ); (ii) H + L 10.84 (0.03), HL + H 9.50 (0.03),  $\text{H}_2\text{L} + \text{H}$  4.20 (0.03),  $\text{H}_3\text{L} + \text{H}$  3.07 (0.03) ([91KKa],  $I = 0.20 \text{ mol L}^{-1} \text{ NaNO}_3$ , 35 °C, potentiometry).

<sup>b</sup>TETA reveals a high affinity toward  $\text{Be}^{2+}$  [82DSa]. The data published for 25 °C and  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$  ( $\lg K_{\text{ML}} = 13.4$ ;  $\lg K(\text{BeL} + \text{H}) = 5.12$ ) are considered reliable, but for critical evaluation an independent measurement is required. The  $\text{Mg}^{2+}$  complex presents a very low stability constant, but it is impossible to recommend a value owing to the large difference between the values reported [91CMa, 82DSa].

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**Table 7** (Continued).

<sup>c</sup>The literature values for the Zn<sup>2+</sup> complex ( $\lg K_{ML}$ ) vary widely as the kinetics of the reaction are slow. In [91CMA], the titration has been performed by a batch method and the reported value is taken as indicative only: 17.6 (0.3);  $I = 0.1 \text{ mol L}^{-1}$  KCl, 25 °C, Conc., gl.

<sup>d</sup>Only one laboratory [91CMB] reports values for Ga<sup>3+</sup> ( $\lg K_{ML} = 19.74$ ) and In<sup>3+</sup> ( $\lg K_{ML} = 21.89$ ); both were derived by potentiometry. Despite the small standard deviation for Ga<sup>3+</sup> (0.01; batch method) and the rather high value for In<sup>3+</sup> these values are considered indicative.

<sup>e</sup>However, the value presented by the same authors for the Fe<sup>3+</sup> complex ( $26.53 \pm 0.01$ ) [91CMB], obtained by competition with NTA is, in comparison with Ga<sup>3+</sup> and In<sup>3+</sup> complexes, too high to be accepted.

<sup>f</sup>Values determined at 80 °C and reported in [86LDB] for several lanthanides ( $I = 1 \text{ mol L}^{-1}$  NaCl, 80 °C, Conc., gl) are accepted as indicative. For Nd<sup>3+</sup>: 14.51 (M + L), 4.56 (ML + H); for Sm<sup>3+</sup>: 14.97 (M + L), 3.90 (ML + H); for Eu<sup>3+</sup>: 15.46 (M + L), 3.77 (ML + H); Gd<sup>3+</sup>: 15.75 (M + L), 3.75 (ML + H); for Dy<sup>3+</sup>: 16.04 (M + L), 3.10 (ML + H); for Er<sup>3+</sup>: 16.49 (M + L), 3.50 (ML + H) and for Yb<sup>3+</sup>: 16.55 (M + L), 2.44 (ML + H).

<sup>g</sup>Enthalpy and entropy changes for the protonation reactions of TETA and for its complexation reactions with Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and earth-alkaline metals (Ca<sup>2+</sup>–Ba<sup>2+</sup>) [84DFa], with Hg<sup>2+</sup> [94KOB], and with La<sup>3+</sup>, Tb<sup>3+</sup>, and Lu<sup>3+</sup> [91KKA] were also determined, but each by a single group.

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