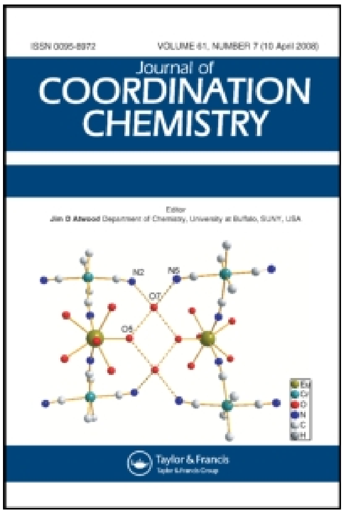

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation, characterization and determination of acid dissociation and stability constants of some acid divalent-metal 1 : 2 nitrilotriacetate complexes

E. R. Souaya[a]; W. G. Hanna[a]; E. H. Ismail[a]; N. E. Milad[a]
[a] Department of Chemistry, Faculty Science, Ain Shams University, Egypt 11566

To cite this Article Souaya, E. R. , Hanna, W. G. , Ismail, E. H. and Milad, N. E.(2004) 'Preparation, characterization and determination of acid dissociation and stability constants of some acid divalent-metal 1 : 2 nitrilotriacetate complexes', Journal of Coordination Chemistry, 57: 10, 825 — 831

To link to this Article: DOI: 10.1080/00958970410001689094

URL: http://dx.doi.org/10.1080/00958970410001689094

J. Coord. Chem., Vol. 57, No. 10, 10 July 2004, pp. 825–831

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PREPARATION, CHARACTERIZATION AND DETERMINATION OF ACID DISSOCIATION AND STABILITY CONSTANTS OF SOME ACID DIVALENT-METAL 1:2 NITRILOTRIACETATE COMPLEXES

E.R. SOUAYA*, W.G. HANNA, E.H. ISMAIL and N.E. MILAD

Department of Chemistry, Faculty Science, Ain Shams University, Egypt 11566

(Received 05 February 2003; Revised 23 May 2003; In final form 27 February 2004)

$H_2[M^{II}(HNTA)_2]\cdot xH_2O$ complexes of eleven divalent metals were prepared. These complexes were characterized *via* elemental analysis, IR spectra, TGA, DTA and ^{1}H NMR. pKa_1 and pKa_2 of these acids were determined together with their $\log\beta_1$ and $\log\beta_2$ as metal complexes.

Keywords: Acid nitrilotriacetate; pKa_1; $\log\beta$

INTRODUCTION

The importance of acid nitrilotriacetates stems from the various uses of H_3NTA and its complexes especially in acid media. An immense number of publications on the use of H_3NTA and its chelates, in different applied fields, are found in the literature. Water and soil studies showed that metals previously adsorbed on a sludge were completely immobilized in the presence of NTA. In addition, NTA is completely degraded during sewage treatment [1]. The removal of lead from contaminated soil using NTA was found to be pH dependent [2]. NTA was also used to ameliorate aluminum toxicity in acid soils [3]. Medical and biological studies showed that aliphatic amine salts of NTA inhibit the growth of bacteria and fungi and have herbicidal activity [4]. H_3NTA and Na_2HNTA increased the deposition of zinc and manganese in chick tibia [5]. Both Al^{III}NTA and Fe^{III}NTA caused bone growth retardation in rats [6]. Fe^{III}NTA was also found to keep iron soluble and highly reactive in blood by providing "free" iron [7]. In rodents, Fe^{III}NTA has been reported to induce a high frequency of adenocarcinoma localized to the proximal tubules of the kidney [8]. Al^{III}NTA exhibited

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*Corresponding author. E-mail: eglals@yahoo.com

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001689094

a similar effect in rats [9]. The mechanism of nephrotoxicity by $Fe^{III}NTA$ was found to be due to selective loss of renal protein [10]. Na_3NTA fed to male rats caused urinary tract toxicity [11].

Despite the large number of publications on H_3NTA and its chelates in different applied fields, very little attention has been directed to structural studies. Tomita and Uneno [12] described the preparation and identification of some solid $HM^{II}NTA$ complexes. The structure of $[Bi(NTA)]\cdot 2H_2O$ was determined by single crystal X-ray studies. It was found that the ligand is completely deprotonated, so the resulting complex is neutral [13]. Single crystal X-ray diffraction was also used to demonstrate the structure of $K_2[VO(O_2)NTA]$ [14]. The vanadium atom was found to have a distorted pentagonal pyramidal environment. The same technique [15] was similarly used to determine the structure of $[Fe_2(NTA)_2(CO_3)O]^{4-}$.

Recently we published a paper [16] on the preparation and characterization of $HM^{II}NTA$ complexes and another [17] on the preparation and characterization of $[Cr_2(NTA)_2]\cdot 3H_2O$ which was found to have a Cr–Cr bond.

The present study describes the preparation and characterization of some acid divalent-metal 1 : 2 nitrilotriacetates, determination of their p*K*a values as acids, and their $\log \beta$ values as metal complexes.

EXPERIMENTAL

All chemicals used are of the A.R. or extra-pure grade.

The calculated amounts of the metal carbonates or basic carbonates of Mg, Ca, Sr, Ba, Zn, Cd, Pb, Mn, Co, Ni and Cu were mixed with H_3NTA in the molar ratio 1 : 2 in about 100 mL of distilled water. The mixture was then heated nearly to boiling point until the reaction was complete. The solution was then left on a low flame until the volume was greatly reduced, followed by cooling in an ice bath where ill-defined crystals separated out on addition of a small amount of ethyl alcohol. The crystals were separated by filtration and recrystallized from boiling water, washed with ethyl alcohol and ether and kept in a vacuum desiccator over silica gel. pKa_1 and pKa_2 values were determined by titrating the aqueous solution of a known weight of the 1 : 2 complex against standard 0.05 N potassium hydroxide solution at $25 \pm 0.2°C$. The method of calculation is fully described by Albert and Serjeant [18]. $\log \beta_1$ and β_2 were determined in exactly the same way as described for the determination of pKa_1 and pKa_2 except for adding 10 mL of 1 M KNO_3 solution in a total volume of 50 mL of the titrate in order to adjust the ionic strength. Calculations were then carried out using the KONST program [19] with its uncertainties and some statistical parameters necessary for the correctness of the fit. Moreover, the data are weighted, i.e. a smaller weight is given to the less accurate regions of the titration curve in which the change of $dE(mV)/dV$ is large. Description of all apparatus and measurements of the present study are fully described elsewhere [17].

RESULTS AND DISCUSSION

The results of elemental analysis of the 1 : 2 complexes of Mg, Ca, Sr, Ba, Zn, Cd, Pb, Mn, Co, Ni and Cu are given in Table I. In order to determine whether the ligand

TABLE I Elemental analysis of 1 : 2 acid divalent-metal nitrilotriacetates

Formula	*M.wt.*	*Solubility* g/L	*M%*		*C%*		*H%*		*N%*	
			Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
$H_2[Mg(HNTA)_2]\cdot 2H_2O$	440.3	1.35712	5.45	5.84	32.70	32.47	4.54	4.01	6.36	6.30
$H_2[Ca(HNTA)_2]\cdot H_2O$	438.0	3.4657	9.13	8.70	32.88	32.50	4.11	4.50	6.39	6.40
$H_2[Sr(HNTA)_2]\cdot H_2O$	485.6	2.6125	18.04	17.72	29.65	29.35	3.71	3.88	5.77	5.91
$H_2[Ba(HNTA)_2]\cdot 0.5H_2O$	517.4	2.6031	26.54	26.82	27.83	27.67	3.10	2.96	5.41	5.18
$H_2[Zn(HNTA)_2]\cdot 0.5H_2O$	445.4	0.4360	14.68	15.52	32.33	32.24	3.59	4.00	6.29	6.27
$H_2[Cd(HNTA)_2]\cdot 0.5H_2O$	492.4	1.9490	22.83	22.50	29.24	28.94	3.25	3.50	5.67	5.50
$H_2[Pb(HNTA)_2]\cdot 0.5H_2O$	587.2	2.6280	35.29	35.40	24.52	24.26	2.72	2.84	4.79	4.46
$H_2[Mn(HNTA)_2]\cdot 0.5H_2O$	435.0	3.4452	12.63	12.60	26.97	26.88	3.68	4.00	6.44	6.63
$H_2[Co(HNTA)_2]\cdot 2H_2O$	475.0	1.4487	12.41	12.60	30.32	30.20	4.21	4.28	5.89	6.00
$H_2[Ni(HNTA)_2]\cdot 3H_2O$	492.7	2.2750	11.92	11.90	29.23	29.12	4.47	4.78	5.68	6.03
$H_2[Cu(HNTA)_2]\cdot 0.5H_2O$	443.5	8.0290	14.33	14.60	32.47	32.32	3.61	4.01	6.31	6.18

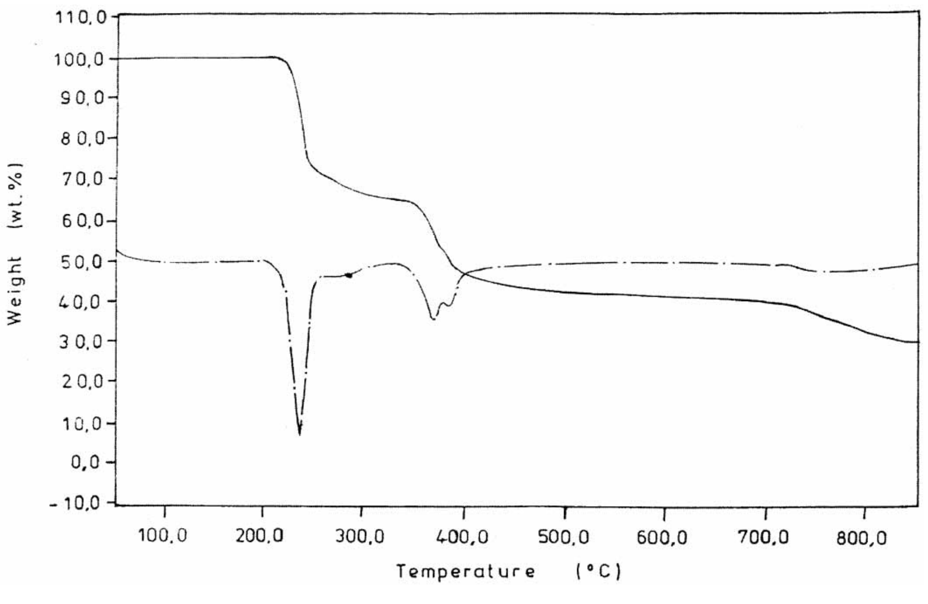


FIGURE 1 T.G.A. and D.T.G. of acid (1 : 2) Ba^{2+} complex.

involved in these complexes is $[NTA]^{3-}$ or $[HNTA]^{2-}$, a simple conductometric titration for a mixture of MCl_2 and H_3NTA in the molar ratio 1 : 1 was carried out against standard 0.05 N KOH solution. Conductivity was found to decrease until 2/3 of the equivalent amount of KOH was added followed by an increase until the equivalence point was reached. This result shows that $MCl_2 + H_3NTA$ gives $[M(HNTA)] + 2HCl$ and not $H[M(NTA)] + 2HCl$ as conductometric titration of the latter products should show a continuous decrease in conductivity throughout the titration against potassium hydroxide.

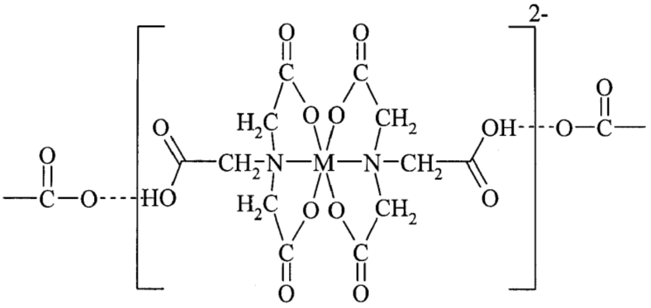
Examination of the thermograms of these complexes (see, for example, Fig. 1) shows a relatively small weight loss below ~200°C for complexes of Ba, Zn, Cd, Pb, Mn and Cu where x (number of water molecules) = 0.5, while those of the remaining five complexes of Mg, Ca, Sr, Co and Ni, where x ranges from 1 to 3 exhibit larger weight losses. We have shown [17] that the parent ligand decomposes, on heating, in two overlapping steps into glycine and maleic acid. Glycine decomposes on further heating into methylamine and carbon dioxide. Maleic acid, on further heating, decomposes into either ethylene and carbon dioxide, or acetylene, carbon monoxide, carbon dioxide and water. The complexes under investigation decompose similarly to H_3NTA. The first and second steps of decomposition of the eleven studied complexes are given in Table II.

While the temperatures of the first weight loss are in the range $225 \pm 25°C$, those of the second weight loss vary widely from 265°C for the zinc complex to 431°C for the copper complex. It may be suggested that both the ionic radius of the corresponding metal and the percent ionic character of the M–O bond are responsible for this phenomenon.

Interesting bands in the IR spectra of the solid complexes are tabulated in Table III. The band at $3020\,cm^{-1}$ is probably due to the stretching frequency of O–H which is lowered *via* hydrogen bonding [21]. Intermolecular hydrogen bonding may explain the extremely low solubility of these complexes compared to those of EDTA.

^{1}H NMR spectra of the ligand and the 1 : 2 calcium and barium complexes are given in Fig. 2. These spectra show two singlets, one at ≈10.15–10.25 ppm and a broad singlet signal ≈10.20–11.60 ppm for the calcium and barium complexes, respectively, as compared to ≈11.20–11.45 ppm for the ligand carboxylic protons. Signals due to protons subject to hydrogen bonding are usually found at ≈10.10–13.40 ppm [5].

In light of the above discussion and keeping in mind that the predominate species of H_3NTA in solutions of the complexes is $[HNTA]^{2-}$ (Fig. 3), the formula of the acid 1 : 2 divalent-metal nitrilotriacetates may have the following structure.



The pKa_1 and pKa_2 values of the eleven acid complexes are given in Table IV. These values reveal moderately strong acids with pKa_1 and pKa_2 for H_3NTA 1.89 and 2.49, respectively [22].

TABLE II Temperatures of first and second weight loss for the acid 1 : 2 divalent-metal nitrilotriacetates

Divalent metal ion	*Mg*	*Ca*	*Sr*	*Ba*	*Zn*	*Cd*	*Pb*	*Mn*	*Co*	*Ni*	*Cu*
1st step °C	213	232	235	237	208	212	200	234	220	254	187
2nd step °C	430	378	352	369	265	374	268	421	350	324	431
Ionic radius Å [20]	0.65	0.92	1.13	1.30	0.74	0.97	0.83	0.79	0.74	0.72	0.65

TABLE III Assignments of the vibrational bands of 1 : 2 acid divalent-metal NTA complexes (cm^{-1})

Complex	*–COOH*	*–COOM–COO*	*O–H*	*M–O*	*M–N*	*O–H···O*
$H_2[Mg(HNTA)_2] \cdot 2H_2O$	1740	1626–1440	3420	386	507	3020
$H_2[Ca(HNTA)_2] \cdot H_2O$	1735	1637–1434	3460	355	536	3020
$H_2[Sr(HNTA)_2] \cdot H_2O$	1733	1616–1440	3460	353	550	3020
$H_2[Ba(HNTA)_2] \cdot 0.5H_2O$	1735	1673–1440	3450	334	534	3020
$H_2[Zn(HNTA)_2] \cdot 0.5H_2O$	1735	1590–1435	3420	355	484	3020
$H_2[Cd(HNTA)_2] \cdot 0.5H_2O$	1735	1578–1435	3420	355	484	3020
$H_2[Pb(HNTA)_2] \cdot 0.5H_2O$	1735	1621–1435	3420	355	484	3020
$H_2[Mn(HNTA)_2] \cdot 0.5H_2O$	1735	1578–1435	3420	355	484	3020
$H_2[Co(HNTA)_2] \cdot 2H_2O$	1733	1579–1429	3400	343	560	3020
$H_2[Ni(HNTA)_2] \cdot 3H_2O$	1733	1581–1431	3400	347	525	3000
$H_2[Cu(HNTA)_2] \cdot 0.5H_2O$	1735	1594–1427	3440	380	563	3000

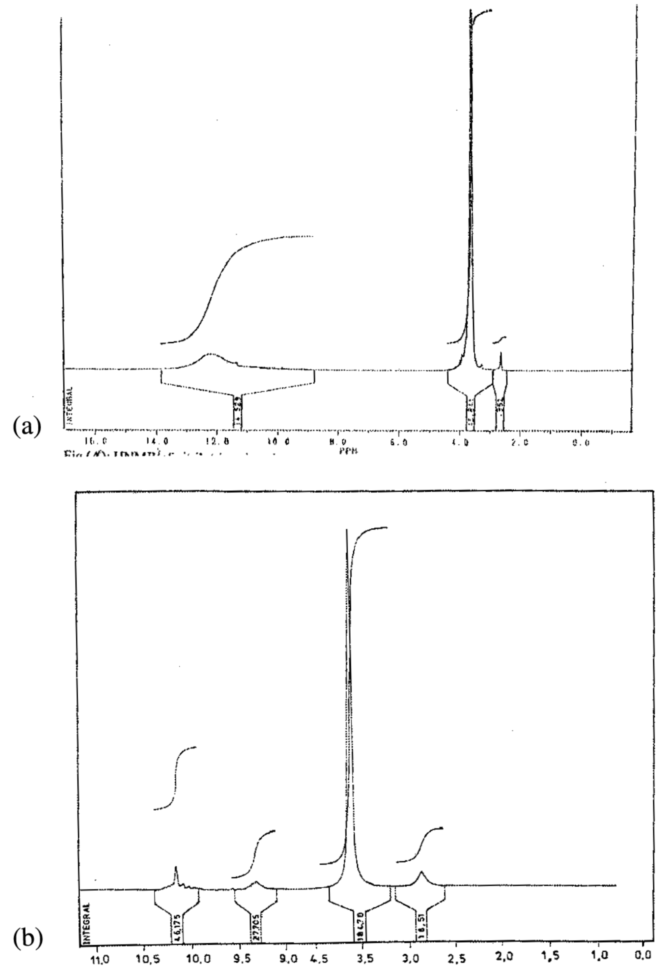


FIGURE 2 H NMR spectra of (a) nitrilotriacetic acid, (b) (1 : 2) $Ca(NTA)_2$ complex, and (c) (1 : 2) $Ba(NTA)_2$ complex.

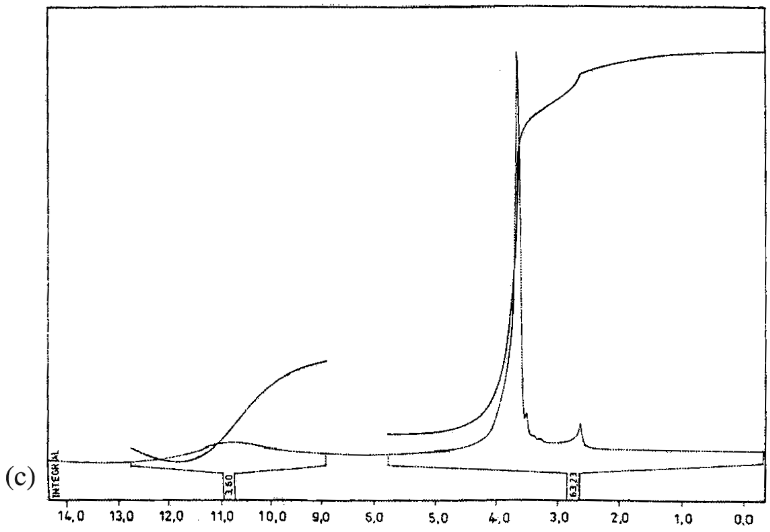


FIGURE 2 Continued.

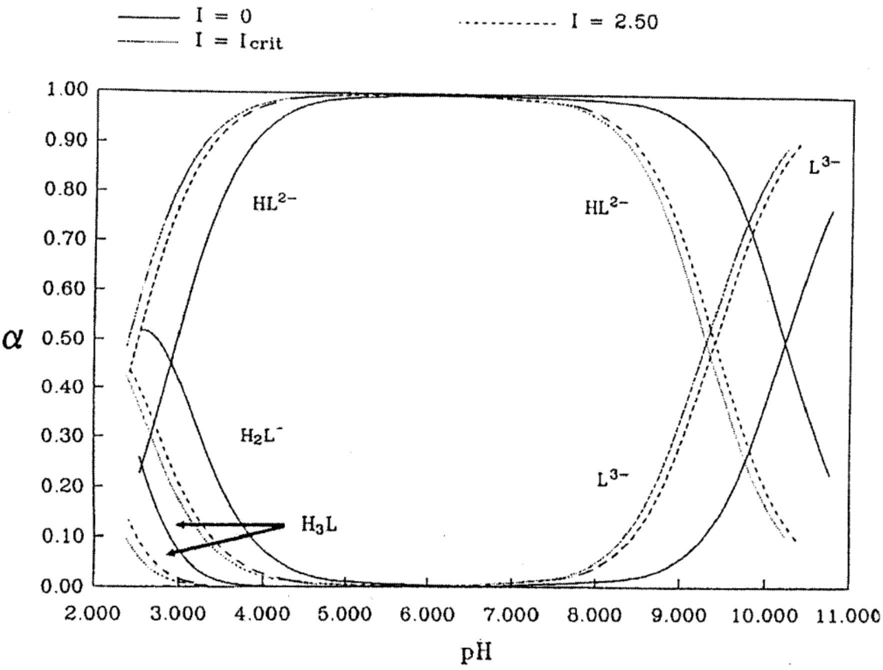


FIGURE 3 Distribution on NTA species in KNO_3 medium.

Log β_1 and log β_2 for the eleven acid complexes are given in Table V. Comparing these values with those recorded in the literature for these metals with NTA we find marked differences in most cases. Literature values are generally higher and log β_1 equals 12.96 for copper [22]. These large differences strongly support our assumption

TABLE IV pKa_1 and pKa_2 of 1 : 2 acid divalent-metal nitrilotriacetates

(1 : 2) M^{II}	*pKa_1*	*pKa_2*
$H_2[Mg(HNTA)_2] \cdot 2H_2O$	2.49	4.63
$H_2[Ca(HNTA)_2] \cdot H_2O$	2.94	3.35
$H_2[Sr(HNTA)_2] \cdot H_2O$	3.18	3.49
$H_2[Ba(HNTA)_2] \cdot 0.5H_2O$	3.11	4.21
$H_2[Zn(HNTA)_2] \cdot 0.5H_2O$	3.19	3.99
$H_2[Cd(HNTA)_2] \cdot 0.5H_2O$	2.50	2.99
$H_2[Pb(HNTA)_2] \cdot 0.5H_2O$	2.78	4.35
$H_2[Mn(HNTA)_2] \cdot 0.5H_2O$	2.94	4.24
$H_2[Co(HNTA)_2] \cdot 2H_2O$	2.76	3.10
$H_2[Ni(HNTA)_2] \cdot 3H_2O$	2.99	3.64
$H_2[Cu(HNTA)_2] \cdot 0.5H_2O$	2.93	3.56

TABLE V Log $\beta 1$ and log β_2 for the 1 : 2 acid divalent-metal nitrilotriacetates

(1 : 2) M^{II}	*log β_1*	*log β_2*
$H_2[Mg(HNTA)_2] \cdot 2H_2O$	7.63	14.64
$H_2[Ca(HNTA)_2] \cdot H_2O$	7.41	14.22
$H_2[Sr(HNTA)_2] \cdot H_2O$	8.79	17.10
$H_2[Ba(HNTA)_2] \cdot 0.5H_2O$	8.74	17.03
$H_2[Zn(HNTA)_2] \cdot 0.5H_2O$	7.95	15.30
$H_2[Cd(HNTA)_2] \cdot 0.5H_2O$	8.41	16.21
$H_2[Pb(HNTA)_2] \cdot 0.5H_2O$	8.35	16.02
$H_2[Mn(HNTA)_2] \cdot 0.5H_2O$	8.05	15.49
$H_2[Co(HNTA)_2] \cdot 2H_2O$	8.58	16.57
$H_2[Ni(HNTA)_2] \cdot 3H_2O$	8.03	15.48
$H_2[Cu(HNTA)_2] \cdot 0.5H_2O$	7.74	14.91

that the values obtained in the present study are those for the effective stability constants where the ligand is in the monoprotonated form [23].

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