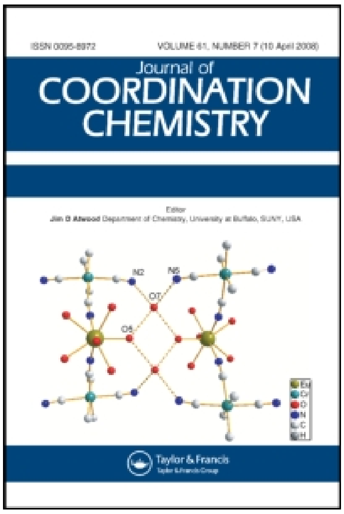

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPLEX SPECIES IN AQUEOUS SOLUTION OF 2,4-TOLUENEDIAMINE-*N, N, N', N'*-TETRAACETIC, 2,6-TOLUENEDIAMINE-*N, N, N'N'*-TETRAACETIC AND 2,6-PYRIDINEDIAMINE-*N, N, N'N'*-TETRAACETIC ACIDS IN THE PRESENCE OF COPPER(II)

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To cite this Article Mederos, A. , Benitez, A. , Rancel, A. , Guerra, R. , Brito, F. , Bazdikian, K. and Bruzal, J.(1986) 'COMPLEX SPECIES IN AQUEOUS SOLUTION OF 2,4-TOLUENEDIAMINE-*N, N, N', N'*-TETRAACETIC, 2,6-TOLUENEDIAMINE-*N, N, N'N'*-TETRAACETIC AND 2,6-PYRIDINEDIAMINE-*N, N, N'N'*-TETRAACETIC ACIDS IN THE PRESENCE OF COPPER(II)', Journal of Coordination Chemistry, 15: 2, 85 — 94

To link to this Article: DOI: 10.1080/00958978608079772

URL: http://dx.doi.org/10.1080/00958978608079772

J. Coord. Chem. 1986, Vol. 15, p. 85–94
0095-8972/86/1502-0085 $18.50/0

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(Received November 13, 1985)

The complex species formed in aqueous solution between Cu(II) and 2,4-toluenediamine-*N,N,N', N'*-tetraacetic acid (2,4-TDTA), 2,6-toluenediamine-*N,N,N',N'*-tetraacetic acid (2,6-TDTA) and 2,6-pyridinediamine-*N,N,N',N'*-tetraacetic acid (2,6-PDTA) were studied at 25° and ionic strength 0,1 M in KCl. The application of the program LETAGROP to the experimental potentiometric data indicates that, upon varying the ligand/metal relationships, the following complex species are formed (ligands, H_4C): 2,4-TDTA($CuHC^-$, CuC^{2-} Cu_2C, Cu_2HC^+ and $Cu_2H_2C^{2+}$); 2,6-TDTA(CuH_2C, $CuHC^-$, CuC^{2-} and Cu_2C); and 2,6-PDTA($CuHC^-$, CuC^{2-} and Cu_2C). 2,4-TDTA, 2,6-TDTA and 2,6-PDTA acids do not form complex species with excess of ligand in the ratio 2/1, as do *m*-phenylenediamine-*N,N,N',N'*-tetraacetic (*m*-PDTA) and *p*-phenylene-diamine-*N,N,N',N'*-tetraacetic (*p*-PDTA) acids.

Keywords: copper, multidentates, stability constants, diamine polycarboxylates

INTRODUCTION

In a previous report[1] it was shown that in aqueous solution *m*-phenelenediamine-*N,N,N',N'*-tetraacetic acid (*m*-PDTA) and *p*-phenylenediamine-*N,N,N',N'*-tetraacetic acid (*p*-PDTA) form, with Cu(II), complex species with excess of ligand (from $Cu(H_2C)_2^{2-}$, deprotonating to CuC_2^{6-}; ligands, H_4C), in the ratio 1/1, CuH_2C, $CuHC^-$ and CuC^{2-}, and with excess of metallic cation Cu_2HC^+ and Cu_2C. This is due to the fact that the diaminepolycarboxylic acid derivatives of *meta* or *para*-phenylenediamines can only coordinate one atom of nitrogen to any one metallic cation. The formation of complexes with excess of ligand on the part of *m*-PDTA acid has been confirmed by studying in aqueous solution the system *m*-PDTA-Be(II).[2] On the contrary, the greater proximity of both nitrogen atoms in the *ortho*-diamine derivatives favours their simultaneous coordination to one and the same cation, as has been established by the X-ray determination of the structure of the complex *o*-PDTA-Co(II) (*o*-PDTA = *o*-phenylenediamine-*N,N,N',N'*-tetraacetic acid),[3] confirming the studies in aqueous solution of the coordinating capacity of the *o*-PDTA acid,[4] 3,4-TDTA (3,4-TDTA = 3,4-toluenediamine-*N,N,N',N'*-tetraacetic acid) and 4-Cl-*o*-PDTA (4-Cl-*o*-PDTA = 4-chloro-1,2-phenylenediamine-*N,N,N',N'*-tetraacetic acid) with Cu(II)[5] and Be(II),[6] where the fundamental complex species are only MHC^- and MC^{2-}. Having

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studied the influence of the position of the atoms of nitrogen on the aromatic ring on the number and type of complex species formed with Cu(II) in acqueous solution by the tetra-*N*-methylcarboxylic acids derived from aromatic diamines, in this work the influence of other factors is studied, such as the presence in the aromatic ring of a methyl group as substituent or replacement of the ring by pyridine. For this purpose we studied the coordinating capacity in aqueous solution of Cu(II) with the acids, derived from *meta*-phenylenediamines, 2,4-toluenediamine-*N,N,N',N'*-tetraacetic acid (2,4-TDTA), 2,6-toluenediamine-*N,N,N',N'*-tetraacetic acid (2,6-TDTA) and 2,6-pyridinediamine-*N,N,N',N'*-tetraacetic acid (2,6-PDTA), and the results obtained are compared with those in the previous report[1] on *m*-PDTA and *p*-PDTA acids.

EXPERIMENTAL

The monosodic salts of 2,4-TDTA acid,[7] 2,6-TDTA acid[8] and 2,6-PDTA acid[9] were prepared as described in the literature. Precautions were taken to maintain an inert atmosphere (argon) and prevent the access of light during the preparation and preservation of the acids and during the study of their solutions, since they are photosensitive and oxidize readily.

The potentiometric titrations were carried out in aqueous solution at ionic strength 0.1 M in KCl and at 25 ± 0.05°. A Radiometer Type PHM-64 potentiometer was used, with a Radiometer G 202 B glass electrode and a K 401 calomel electrode. The cell constants were determined according to the method of Biedermann and Sillen.[10] Carbonate-free sodium hydroxide solution was prepared according to the procedure of Sillen[11] and standardized against potassium hydrogen phthatate. The Cu(II) solution (in the form of the chloride) was evaluated electrolytically[12] and by titration with EDTA[13] (KCl, $CuCl_2$ and NaOH, Merck, analytical grade).

Measurements were taken of the ligands only, at an approximate concentration of 1 mM, and of the ligands in the presence of Cu(II): concentrations of Cu(II) of 0.5, 1.0 and 5.0 mM were studied, varying the concentration of monosodic salt of 2,4-TDTA acid in the ligand/metal ratios 2/1, 1/1 and ½, concentrations of ligand of 0.5, 1.0 and 1.5 mM, varying the concentration of Cu(II) in the ratios 2/1, 1/1 and 1/2, for 2,6-TDTA acid, and concentrations of ligand of 0.5, 1.0 and 1.6 mM, in the ligand/metal ratios 3/1, 1/1 and 1/3, for 2,6-PDTA acid.

Data treatment

The experimental potentiometric data were analysed by means of the NERNST/LETA/GRAFICA version[14] of the LETAGROP Program,[15] based on a generalised form of the least-squares method that establishes the best model and best values of the β_{pqr} constants, minimizing the function $U = \Sigma(Z_{exp} - Z_{calc})^2$, Z being the average number of dissociated protons for the total concentration of ligand (Z_C) or for the total concentration of metal (Z_B). The LETAGROP calculations also give standard deviations $\sigma(Z)$ and $\sigma(\log \beta_{pqr})$.[16] The computations were performed on a Burroughs 6700 computer (Facultad de Ciencias, Universidad Central de Venezuela, Caracas). It was found that under the experimental conditions used hydrolysis of Cu(II) is negligible.

RESULTS AND DISCUSSION

Ionization Constants of the Acids

From the values obtained for the constants β_{pr} corresponding to the equilibria (*1*)

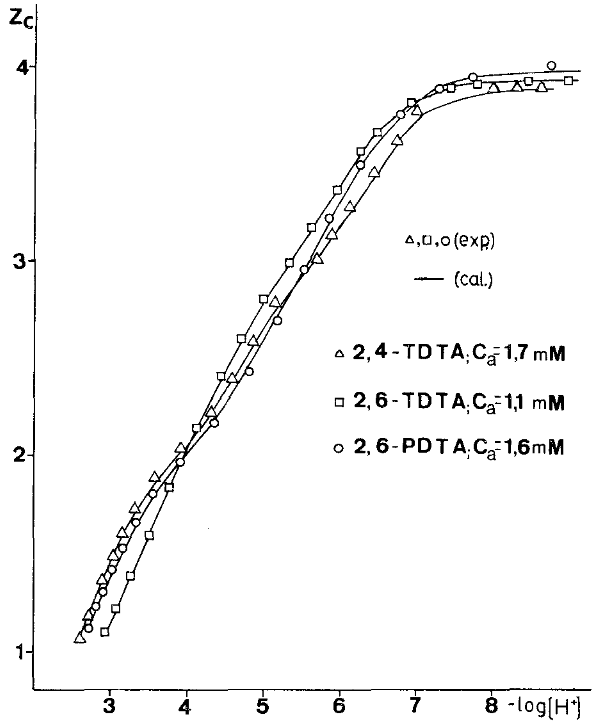

FIGURE 1 Z_C(−log [H $^+$]) curves corresponding to 2,4-TDTA, 2,6-TDTA and 2,6-PDTA acids. Full curves have been calculated using the set of proposed constants β_{pr} in Table I

$$p\,H^+ + r\,H_4C \rightleftharpoons H_p(H_4C)_r^{p+} \qquad (1)$$

the ionization constants of the acids K_i, given in Table I, could readily be determined. For comparison purposes, values for *m*-PDTA acid[1], at the same ionic strength and temperature, are also included.

The validity of the values found for the constants β_{pr} is proven in Figure 1 by excellent agreement between the experimental curves Z(−log [H $^+$]) and those calculated from the β_{pr} values given in Table I. The values of pK_i for 2,4-TDTA acid are in good agreement with those found by us in previous work.[7]

The values of pK_1 and pK_2 correspond to protons situated fundamentally over carboxylic groups, whereas the values of pK_3 and pK_4 correspond to fundamentally betainic protons.[7–9, 17,18] The non-protonation pyridinic nitrogen atom in 2,6-PDTA acid is also apparent in its UV spectrum in aqueous solution and as a function of the pH.[9] This behaviour of 2,6-PDTA acid is exceptional, and is probably due to the fact that the presence of the four CH_2 groups of the *N*-methylcarboxylic groups prevents the proton from stabilizing on the pyridinic nitrogen atom in the species HC^{3-}, by means of steric repulsions. On the contrary, the species HC^+ in the diamines 2,6-pyridinediamine and 2,5-pyridinediamine (log $K_1 = 6.62$ and 6.58, respectively), HC^- in the 2,6-pyridinediamine-*N*,*N*′-diacetic acid (2,6-PDDA) with $pK_2 = 6.97$, and HC^{3-} in 2,5-pyridinediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (2,5-PDTA) with $pK_4 = 6.96$ (all constants at 25°; $I = 0.1$ in KCl), are protonated on the pyridinic nitrogen atom,

TABLE I

Ionization Constants of 2,4-TDTA, 2,6-TDTA and 2,6-PDTA acids at 25° and I = 0.1 M in KCl

			$-\log \beta_{pr}$		
pr	2,4-TDTA	pr	2,6-TDTA	pr	2,6-PDTA
		11	−1.96 ± 0.03		
11	−2.22 ± 0.03	−11	2.25 ± 0.04	−11	2.13 ± 0.24
−11	2.94 ± 0.03	−21	5.66 ± 0.04	−21	5.18 ± 0.16
−21	7.73 ± 0.04	−31	10.18 ± 0.05	−31	10.12 ± 0.19
−31	14.32 ± 0.05	−41	16.31 ± 0.07	−41	16.35 ± 0.18
a	2		2		1
b	83		89		63
c	0.016		0.029		0.032
d	2.0–8.7		1.6–10.3		2.7–11.0

a = Number of titrations; b = Number of experimental points; c = Standard deviations $\sigma(Z)$; d = $-\log[H^+]$ range. (The use of the monosodic salt of 2,5-TDTA acid led to the calculated real values of p of 1, -1, -2 and -3, respectively)

		pK_i		
Equilibrium	2,4-TDTA	2,6-TDTA	2,6-PDTA	*m*-PDTA[1]
H_5C^+/H_4C		1.96		
H_4C/H_3C^-	2.22	2.25	2.13	2.11
H_3C^-/H_2C^{2-}	2.94	3.41	3.05	2.79
H_2C^{2-}/HC^{3-}	4.79	4.52	4.94	5.00
HC^{3-}/C^{4-}	6.59	6.13	6.23	5.75

TABLE II

Stability Constants of 2,4-TDTA, 2,6-TDTA and 2,6-PDTA acids with Cu(II) at 25° and I = 0.1 M in KCl.

			$-\log \beta_{pqr}$		
pqr	2,4-TDTA	pqr	2,6-TDTA	pqr	2,6-PDTA
−211	2.518 ± 0.075	−211	2.267 ± 0.037		
−311	6.838 ± 0.069	−311	5.493 ± 0.012	−311	5.029 ± 0.016
−121	−2.904 ± 0.261	−411	10.208 ± 0.022	−411	9.671 ± 0.038
−221	−0.549 ± 0.205	−421	6.610 ± 0.053	−421	6.753 ± 0.121
−321	2.833 ± 0.129				
a	9		9		9
b	181		193		120
c	0.057		0.017		0.021
d	2.4–8.1		2.7–7.2		2.5–6.5

a = Number of titrations; b = Number of experimental points; c = Standard deviations $\sigma(Z)$; d = $-\log[H^+]$ range. (The use of the monosodic salt of 2,4-TDTA acid led to real values of pqr of -211, -311, -121, -221, -321, respectively).

			log K		
Equilibrium	p-PDTA	m-PDTA	2,4-TDTA	2,6-TDTA	2,6-PDTA
$H_2C^{2-} + Cu^{2+}/CuH_2C$	4.69	4.47		3.39	
$HC^{3-} + Cu^{2+}/CuHC^-$	6.95	6.65	5.21	4.68	5.10
$C^{4-} + Cu^{2+}/CuC^{2-}$	8.16	8.22	7.48	6.11	6.68
$H_2C^{2-} + 2Cu^{2+}/Cu_2H_2C^{2+}$			5.85		
$HC^{3-} + 2Cu^{2+}/Cu_2HC^+$	8.94	8.82	8.28		
$C^{4-} + 2Cu^{2+}/Cu_2C$	12.82	12.07	11.48	9.71	9.60
$CuHC^- + Cu^{2+}/Cu_2HC^+$	1.99	2.17	0.52		
$CuC^{2-} + Cu^{2+}/Cu_2C$	4.66	3.85	4.00	3.60	2.92

which is the most basic.[9] The order of basicity for the species HC^{3-}, 2,4-TDTA > 2,6-TDTA > *m*-PDTA is explained by the inductive electron-donor nature of the radical CH_3, and by the greater repulsive steric effects of this radical in 2,6-TDTA acid, on being situated in an *ortho* position with regard to both nitrogen atoms.

Stability Constants of the Complexes Formed

The analysis of the experimental data for each of the three ligand-metal systems by the NERNST/LETA/GRAFICA version[14] of the LETAGROP program[15] allowed us to calculate the β_{pqr} constants for the complex species formed for each ligand, defined by means of the equilibria (*2*).

$$p\,H^+ + q\,Cu^{2+} + r\,H_4C \rightleftharpoons H_pCu_q(H_4C)_r^{(P+2q)+} \qquad (2)$$

The model that best fits the experimental results for each ligand is that which corresponds to the complex species indicated in Table II. The validity of the same is proven in Figures 2, 3 and 4, where an excellent fit can be observed between the experimental curves $Z(-\log[H^+])$ and those calculated from the β_{pqr} values given in Table II. Although models were tested that included the possible presence of complex species with excess of ligand, the results indicate that they are not present in significant amounts.

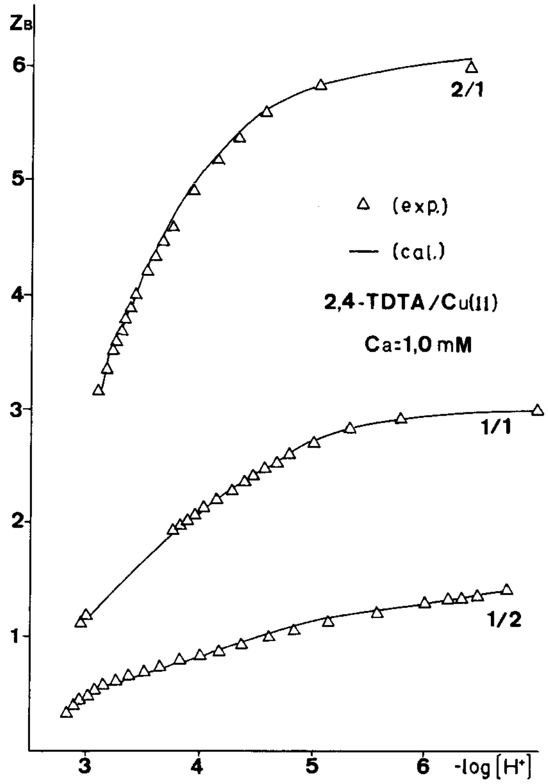

FIGURE 2 $Z_B(-\log[H^+])$ curves of the system 2,4-TDTA-Cu(II). Full curves have been calculated using the set of proposed constants β_{pqr} in Table II

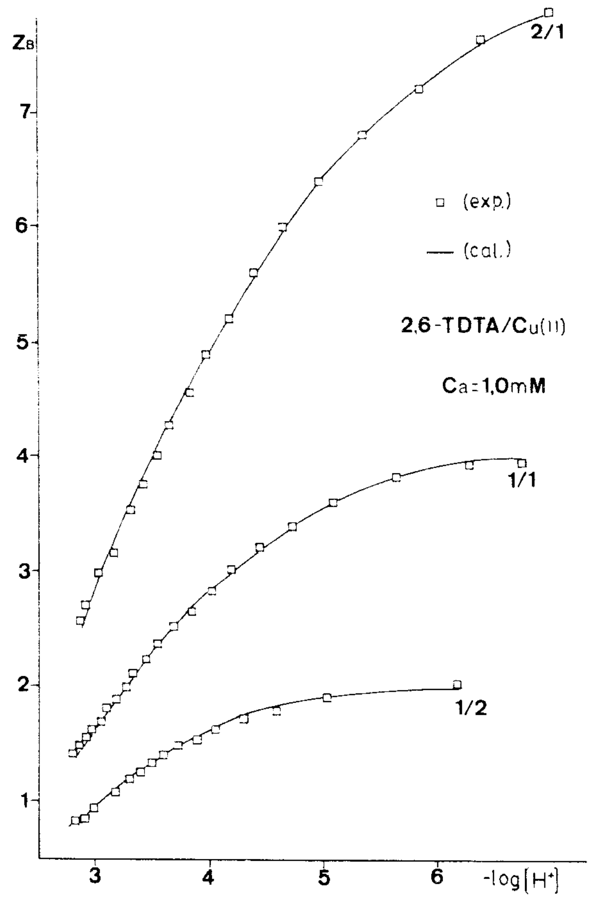

FIGURE 3 Z_B(-log[H^+]) curves of the system 2,6-TDTA-Cu(II). Full curves, calculated using the constants β_{pqr} in Table II

From the β_{pqr} constants and taking into account the β_{pr} constants of the acids given in Table I, the stability constants of the complex species formed can readily be calculated, according to the equilibria given in Table II. For comparison purposes, in this series of ligands, they are also contrasted with data for *m*-PDTA and *p*-PDTA acids.[1]

The values of pK_i corresponding to the ionization of the protonated complex species, and the equilibria (*3*)

$$CuHC^- + Cu^{2+} \rightleftharpoons Cu_2C + H^+ \qquad (3)$$

readily obtained from Tables I and II, are given in Table III.

The most striking characteristic of 2,4-TDTA, 2,6-TDTA and 2,6-PDTA acids, as compared with *m*-PDTA and *p*-PDTA acids,[1] is the practical non-formation in aqueous solution with Cu(II) of complex species with an excess of ligand in the ratio 2/1. *m*-PDTA and *p*-PDTA acids formed these species with an excess of ligand when two potentially tridentate iminodiacetic groups of different ligands[1] coordinated to one

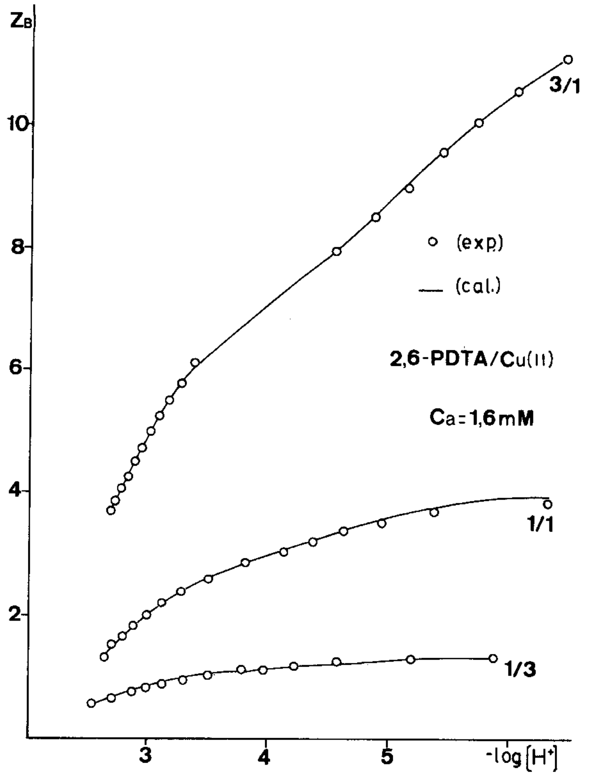

FIGURE 4 $Z_B(-\log[H^+])$ curves of the system 2,6-PDTA-Cu(II). Full curves, calculated using the constants β_{pqr} in Table II

TABLE III
Ionization Constants of the Protonated Complex Species at 25° and I = 0.1 M in KCl

	pK_i				
Equilibrium	p-PDTA	m-PDTA	2,4-TDTA	2,6-TDTA	2,6-PDTA
$CuH_2C/CuHC^-$	2.61	2.82		3.23	
$CuHC^-/CuC^{2-}$	4.90	4.18	4.32	4.71	4.65
$Cu_2H_2C^{2+}/Cu_2HC^+$			2.36		
Cu_2HC^+/Cu_2C	2.23	2.50	3.39		
Equilibrium (*3*)	0.24	0.33	0.32	1.10	1.73

and the same metallic cation. The non-formation of these complex species ($CU(H_2C)_2^{2-}$ to CuC_2^{6-}) in 2,4-TDTA, 2,6-TDTA and 2,6-PDTA acids must be attributed to the presence of the methyl radical as substituent on the aromatic ring in the first two, and to the presence of a pyridinic nitrogen atom in the aromatic ring in 2,6-PDTA acid. The methyl radicals of different ligands bring repulsive steric effects to bear on complexes with a 2/1 excess of ligand in 2,4-TDTA and 2,6-TDTA acids that hinder the stability of these species. In 2,6-PDTA acid, since the conformation of the iminodiacetic groups is the same as in *m*-PDTA acid, it must be admitted that the coordination of the N atom of the pyridinic ring to an atom of Cu in the species Cu^{2-} or $CuHC^-$ prevents, by steric repulsion, the stability of the species with excess ligand CuC_2^{6-} or $Cu(HC)_2^{4-}$.

The data from the literature[19–23] show that the coordinating capacity of pyridines or aminopyridines *versus* Cu(II) and other cations is weak (pyridine log K = 2.56 at 25° and I = 0.1; 2-aminopyridine, log K = 1.75 at 25° and I = 0.6; 3-methyl-2-aminopyridine, log K = 1.91 at 25° and I = 0.6; *etc.*) From these data it can be deduced that in acid 2,6-PDTA, Cu(II) is not bonded to the pyridinic nitrogen of the ring only, and a simultaneous coordination of the pyridinic N of the ring and of the nitrogen of the iminodiacetic group is highly unlikely. It seems therefore that the most probable structure for the complex CuHC is that shown in Figure 5. The acidity of this species (Table III) is consistent with a structure that is fundamentally betainic for the proton, neutralization of which leads to the species CuC^{2-}. The lesser stability of the complexes $CuHC^-$ and CuC^{2-} in 2,6-PDTA acid (Table II), despite the fact that the pyridinic nitrogen is more basic, with respect to those corresponding to *m*-PDTA acid in which the Cu(II) is bonded to an iminodiacetic group, is accounted for by the greater length of the 7-membered chelate rings (Figure 5) with respect to the 5-membered chelate rings in the *m*-PDTA complexes, which are more stable for this cation.[24] The shift of the proton in the species $CuHC^-$ by another Cu(II) to give the species Cu_2C is very pronounced (equilibrium (*3*), Table III, for 2,6-PDTA acid), which seems to indicate that in the species Cu_2C the second Cu(II) is coordinated to the iminodiacetic group. The permanence of the former, coordinated to the pyridinic nitrogen as in Figure 5, explains the smaller stability of this species with respect to that corresponding to *m*-PDTA acid, for identical reasons (*vide supra*).

The acidity values of the species CuHC (Table III) when compared with pK_3 for the acids (Table I) show that for all the acids studied the proton in the species CuHC is a fundamentally betainic one as seen in Figure 5. The metallic cation is coordinated to the other iminodiacetic group (except in 2,6-PDTA, Figure 5). On the other hand the other proton in the species CuH_2C corresponds to one situated fundamentally on a carboxylic group, as can be deduced from the values given in Table III, upon comparison with pK_2 of the acids (Table I). In 2,4-TDTA and 2,6-PDTA acids this species is formed at $pH < 2.5$,[7,9] below those studied in this work. The calculations indicate that, at least at the concentrations studied, the complexes in the ratio 1/1 are not dimerized to those with the ratio 2/2, as postulated for *m*-PDTA acid.[25]

The expulsion of the proton bonded to the N atom in the species $CuHC^-$ by another Cu(II) to form the bimetallic species Cu_2C, is essentially complete for all the acids (equilibrium (*3*), Table III). This result is consistent with the conductimetric titration curves in the ligand/metal ratios 1/1 and 1/2.[7–9] The most probable structure for this species Cu_2C, with each metallic atom coordinated to an iminodiacetic group, is

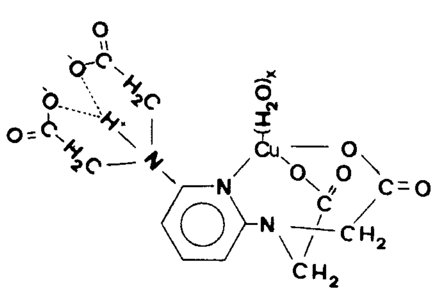

FIGURE 5 Structure proposed for the complex $CuHC^-$ in the 2,6-PDTA acid

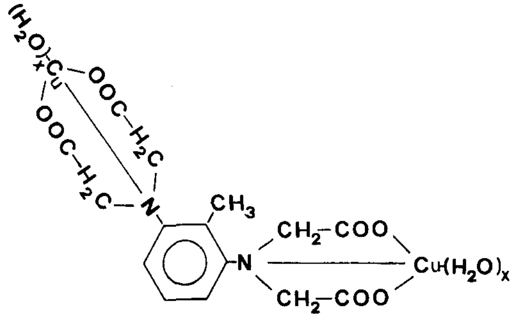

FIGURE 6 Structure proposed for the complex Cu_2C in the 2,6-TDTA acid

similar to that in Figure 6 for all the acids except 2,6-PDTA (Cu_2C for 2,6-TDTA acid). The monoprotonated bimetallic species Cu_2HC^+ found for 2,4-TDTA acid was also found for *m*-PDTA and *p*-PDTA acids.[1] It is interesting to note that the diprotonated species $Cu_2H_2C^{2+}$ was also found for 2,4-TDTA acid. The values calculated for the acidity of these species (Table III) indicate that these protons are fundamentally carboxylic, similar to that in Figure 7 for the species Cu_2HC^+ in 2,4-TDTA acid. In the species $Cu_2H_2C^{2+}$, the other protonated carboxylic group would be on the other iminodiacetic group. However, some type of interaction of these carboxylic protons cannot be excluded, either with nitrogen atoms or the π system of the aromatic ring, if it is taken into account that these are cationic species which would make the mere presence of these carboxylic protons more unstable. Confirmation of this supposition requires other experimental studies in aqueous solution such as IR or ^1H NMR measurements.

The values of log K (Table II) indicate the order of coordinating capacity *m*-PDTA > 2,4-TDTA > 2,6-TDTA. This order is attributed to the repulsive steric effects of the methyl radical on the metallic cation. Thus, the most drastic decrease of the complexing strength in 2,6-TDTA acid is due to the presence of the methyl radical in an *ortho* position with respect to both nitrogen atoms, leading to greater steric respulsions (Figure 6). This order of coordinating capacity is analogous to that found with other divalent alkaline earth and transition metal cations.[7,8,19]

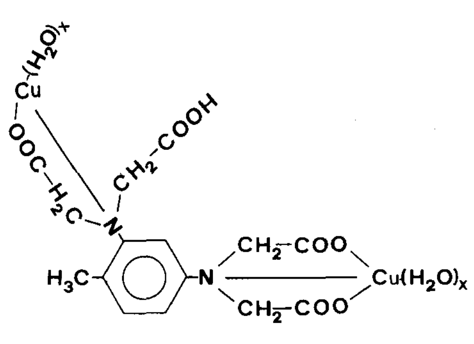

FIGURE 7 Structure proposed for the complex Cu_2HC^+ in the 2,4-TDTA acid

REFERENCES

1. A. Mederos, J.M. Felipe, F. Brito and K. Bazdikian, *J. Coord. Chem.*, in press.
2. A. Mederos, S. Dominguez, M. Hernández-Padilla, F. Brito and E. Chinea, *Bol. Soc. Quim. Perú*, **50,** 277 (1984).
3. E.F.K. McCandlish, T.K. Michael, J.A. Neal, E.C. Lingafelter and N.J. Rose, *Inorg. Chem.*, **17,** 1383 (1978).
4. N. Nakasuka, M. Kunimatsu, K. Matsumura and M. Tanaka, *Inorg. Chem.*, **24,** 10 (1985).
5. A. Mederos, J.M. Felipe, F. Brito and K. Bazdikian, to be published.
6. A. Mederos, J.M. Felipe, M. Hernández-Padilla, F. Brito, E. Chinea and K. Bazdikian, *J. Coord. Chem.*, in press.
7. A. Mederos, J.V. Herrera, M. Modolell, A. Rancel and J.M. Felipe, *An. Quim.*, **80B,** 213 (1984).
8. A. Mederos, J.V. Herrera, A. Rancel and A. Benitez, to be published; A. Rancel, Thesis, University of La Laguna, 1984.
9. A. Mederos, J.V. Herrera, A. Benitez and A. Rancel, *An. Quim.*, to be published; A. Benitez, Thesis, University of La Laguna, 1984.
10. G. Biedermann and L.G. Sillen, *Arkiv Kemi*, **5,** 425 (1953).
11. F. Brito and N. Ingri, *An. Quim.*, **56B,** 165 (1960).
12. I.M. Kolthoff, E.B. Sandell, E.J. Meehan and S. Bruckenstein, *Quantitative Chemical Analysis*, 4th ed., McMillan, London (1969), p. 1042
13. G. Schwarzenbach, *Las complexonas en el Análisis Químico*, Atlas, Madrid (1959).
14. F. Brito and J.M. Goncalves, Project Num. 51.78.31-S1-1228, CONICIT (1981), Caracas, Venezuela.
15. R. Arnek, L.G. Sillen and O. Wahlberg, *Arkiv Kemi*, **31,** 353 (1969).
16. L.G. Sillén, *Acta Chem. Scand.*, **16,** 159 (1962); L.G. Sillén and B. Warnqvist, *Arkiv Kemi*, **31,** 341 (1969).
17. A. Mederos, A. Rodriguez González and B. Rodriguez Rios, *An. Quim.*, **69,** 601 (1973).
18. A. Mederos, F.G. Manrique, J.V. Herrera, M. Alvarez-Romero and J.M. Felipe, *An. Quim.*, in press.
19. A.E. Martell and R.M. Smith, *Critical Stability Constants, Vol 1: Amino Acids*, Plenum Press, New York (1974).
20. R.M. Smith and A.E. Martell, *Critical Stability Constants, Vol 2: Amines*, Plenum Press, New York (1975).
21. A.E. Martell and R.M. Smith, *Critical Stability Constants, Vol 5: First Supplement*, Plenum Press, New York (1982).
22. D.D. Perrin, *Stability Constants of Metal-Ion Complexes, Part B, Organic Ligands*, Pergamon Press, Oxford (1979).
23. E.P. Serjeant and B. Dempsey, *Ionization Constants of Organic Acids in Aqueous Solution*, Pergamon Press, Oxford (1979).
24. R.C. Courtney, S. Chabereck and A.E. Martell, *J. Am. Chem. Soc.*, **75,** 4814 (1953).
25. S. González García and F.J. Sánchez Santos, *An. Quim.*, **72,** 148, 153 (1976), and **77B,** 175 (1981).