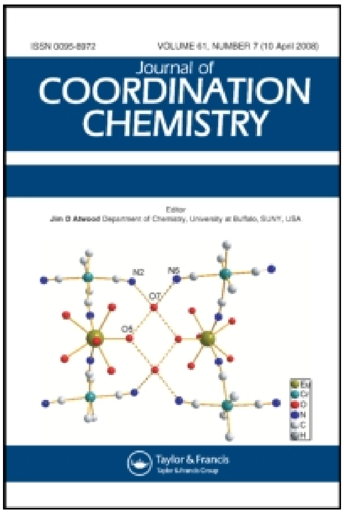


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Complex Species of 2,5-Toluenediamine-N,N,N',N'-Tetraacetic Acid with Copper(II) in Aqueous Solution

F. Brito[a]; P. Gili[b]; A. Mederos[b]; S. Dominguez[b]; A. E. Rivero[b]
[a] Laboratorio de Equilibrios en Solutiön, Escuela de Quimica. Facullad de Ciencias, Unirersidad Central de Venezuela, Caracas, Venezuela [b] Deparlamento de Quimica Inorganica, Universidad de La Laguna, Tenerife, Canary Islands, Spain

To cite this Article Brito, F. , Gili, P. , Mederos, A. , Dominguez, S. and Rivero, A. E.(1990) 'Complex Species of 2,5-Toluenediamine-N,N,N',N'-Tetraacetic Acid with Copper(II) in Aqueous Solution', Journal of Coordination Chemistry, 21: 1, 29 — 37

To link to this Article: DOI: 10.1080/00958979009408180

URL: http://dx.doi.org/10.1080/00958979009408180

J. Coord. Chem. 1990, Vol. 21, pp. 29–37
Reprints available directly from the publisher
Photocopying permitted by license only

COMPLEX SPECIES OF 2,5-TOLUENEDIAMINE-N,N,N',N'-TETRAACETIC ACID WITH COPPER(II) IN AQUEOUS SOLUTION

F. BRITO

Laboratorio de Equilibrios en Solución, Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela.

P. GILI, A. MEDEROS,* S. DOMINGUEZ and A. E. RIVERO

Departamento de Química Inorgánica, Universidad de La Laguna, Tenerife, Canary Islands, Spain.

(Received May 7, 1989; in final form August 8, 1989)

The complex species formed in aqueous solution between 2,5-toluenediamine-*N,N,N',N'*-tetraacetic acid (2,5-TDTA) and Cu(II) were studied at 25°C and ionic strength 0.1 M in KCl. Potentiometric investigations were carried out at ligand:metal ratios 2:1 and 1:1 (C_M = 1.5 mM and 2 mM), and ratios 1:3, 1:4 and 1:5 (C_L = 2 mM). The applications of the least-squares computer program LETAGROP to the experimental potentiometric data, in the pH range studied (2.29–8.74), indicate that the following complex species are formed (ligand H_4C): $[CuHC]^-$, $[CuC]^{2-}$, $[Cu(H_2C)_2]^{2-}$, $[Cu(HC)_2]^{4-}$ and Cu_2C. 2,5-TDTA acid, as does *para*-phenylenediamine-*N,N,N',N'*-tetraacetic acid (*p*-PDTA), forms complexes with excess of ligand in the ratio 1:1, or with excess metallic cation. This is due to the fact that the diaminepolycarboxylic acid derivatives of *meta* or *para*-phenylenediamines can only coordinate an atom of nitrogen to any one metallic cation. The values of log K indicate the order of coordinating capacity *p*-PDTA > 2,5-TDTA. This order is attributed to repulsive steric effects between the methyl radical and the metallic cation.

Keywords: Copper(II), toluenediamine, multidentates, stability constants

INTRODUCTION

In a previous report[1] it was shown that in aqueous solution *p*-phenylenediamine-*N,N,N',N'*-tetraacetic acid (*p*-PDTA) and *m*-phenylenediamine-*N,N,N',N'*-tetraacetic acid (*m*-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 *para* or *meta*-phenylenediamines can only coordinate one nitrogen to any one metallic cation. In another study,[2] the influence of a methyl group as a substituent on the aromatic ring in tetramethylcarboxylic acids derived from *meta*-phenylenediamines was explored. A study was performed of the coordinating capacity in aqueous solution of Cu(II) with 2,4-toluenediamine-*N,N,N',N'*-tetraacetic (2,4-TDTA) and 2,6-toluenediamine-*N,N,N',N'*-tetraacetic (2,6-TDTA) acids. It was found that 2,4-TDTA and 2,6-TDTA acids do not form Cu(II) complex species with an excess of ligand in the ratio

---

* Author for correspondence.

2/1 to any significant extent. *m*-PDTA acid and *p*-PDTA acids formed these species with an excess of ligand, when two potentially terdentate iminodiacetic groups of different ligands[1] coordinated to one and the same metallic cation. The non-formation of the complex species ($[Cu(H_2C)_2]^{2-}$ to $[CuC_2]^{6-}$) for 2,4-TDTA and 2,6-TDTA acids must be attributed to the presence of the methyl radical as a substituent on the aromatic ring. 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 such that hinder the stability of these species. In this work, a study is reported of the influence of the methyl group on the formation of these species with excess of ligand in tetramethylcarboxylic acids derived from *para*-phenylenediamines; we have studied the coordinating capacity in aqueous solution (25°C; $I = 0.1$ M in KCl) of Cu(II) with 2,5-toluenediamine-*N,N,N′,N′*-tetraacetic acid (2,5-TDTA). Previous studies of the system Cu(II)-2,5-TDTA,[3] did not permit analysis of the possible presence of the above mentioned species.

EXPERIMENTAL

2,5-TDTA acid was obtained by following a slight modification of the method developed by B. Rodriguez Rios and A. Mederos.[4] After separation of CdS, the solution was concentrated on a rotavapor and the concentrated solution was transferred to a small crystallization vessel and stored for two months in a desiccator under vacuum with P_4O_{10}. For purification purposes, it was again dissolved in water, filtered, and the filtrate concentrated once more on a rotavapor. The concentrated solution was again transferred to a small crystallization vessel and stored for three months in a desiccator under vacuum with P_4O_{10}. Precautions were taken to maintain an inert atmosphere (argon) and to prevent the access of light during the preparation and preservation of the acid and during the study of its solutions, since it is photosensitive and oxidizes readily.

The preparation and evaluation of the solutions of Cu(II), HCl, NaOH and KCl were performed as reported in earlier reports.[1,2,5,6] Likewise, the apparatus and titration procedures employed are the same as described previously.[1,2,5,6]

Measurements were made of the ligand, alone, with HCl and NaOH, respectively ($C_L = 2$ mM), and of the ligand in the presence of Cu(II) at ligand:metal ratios 2:1 and 1:1 ($C_M = 1.5$ mM and 2 mM) and ratios 1:3, 1:4 and 1:5 ($C_L = 2$ mM).

The experimental potentiometric data were analysed by means of the NERNST/LETA/GRAFICA version of the LETAGROP program as used earlier.[1,2,5,6]

The presence of the $[Cu_2(OH)_2]^{2+}$ species, which is the major hydrolytic species of Cu(II),[7] has been taken into account in the calculations for the ligand–Cu(II) systems. It was found that pKw = 13.74, in excellent agreement with reported data.[8]

Electronic spectra

Ultraviolet spectra were recorded in aqueous solution on a Perkin-Elmer 550 S spectrophotometer. Measurements were taken of the ligand ($C_L = 10^{-5}$ mM and 10^{-4} mM at pH 2, 3.5, 4, 6 and 10), and of the ligand in the presence of Cu(II) at ligand:metal ratio 1:1 ($C_L = 10^{-5}$ mM at pH 2, 3.5, 6 and 8.5; and $C_L = 10^{-4}$ mM at pH 2, 4 and 6).

RESULTS AND DISCUSSION

Ionization constants of the acids

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

$$pH^+ + rH_4C \rightleftharpoons [H_p(H_4C)_r]^{p+} \qquad (1)$$

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

TABLE I

Ionization constants for 2,5-TDTA acid (25°C, $I = 0.1$ M in KCl).

pr	$-\text{Log}\ \beta_{pr}$	Equilibrium	pKi	pKi(p-PDTA)[1]
11	-1.97 ± 0.02	$H_5C^+ \rightleftharpoons H_4C$	1.97	
−11	1.85 ± 0.02	$H_4C \rightleftharpoons H_3C^-$	1.85	1.83
−21	4.29 ± 0.01	$H_3C^- \rightleftharpoons H_2C^{2-}$	2.44	2.87
−31	8.84 ± 0.03	$H_2C^{2-} \rightleftharpoons HC^{3-}$	4.55	4.87
−41	16.05 ± 0.03	$HC^{3-} \rightleftharpoons C^{4-}$	7.21	6.11

No. of titrations/No. of experimental points	2/84
Standard deviation [$\sigma(Z)$]	0.017
$-\text{Log}\ [H^+]$ range	1.87–10.51

The values of pK_0, 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.[9–12] For comparative purposes, Fig. 1 shows the distribution of species as a function of $-\log[H^+]$ for *p*-PDTA and 2,5-TDTA acids (calculated in accordance with the values of $-\log \beta_{pr}$ given in Ref. 1 for *p*-PDTA and given in Table I, for 2,5-TDTA, respectively). For *p*-PDTA acid the diprotonated species H_2C^{2-}, with a fundamentally betainic structure, is the most important species. In 2,5-TDTA acid, the introduction of a methyl group in the aromatic ring increases the electronic density on the nitrogen atom *ortho* to the methyl group and produces an asymmetry in the distribution of electronic charge, such that the monoprotonated species HC^{3-}, also having a fundamentally betainic structure, is the most important species (Fig. 2).

The protonation of the nitrogen atoms in aqueous solution is confirmed by means of the study of ultraviolet spectra as a function of the pH. These spectra present, in the expected order of energy and intensity, the three bands corresponding to the aromatic ring,[9–12] ${}^1E_{1u} \longleftarrow {}^1A_{1g}$, ${}^1B_{1u} \longleftarrow {}^1A_{1g}$ and ${}^1B_{2u} \longleftarrow {}^1A_{1g}$, respectively. The band with least intensity and energy, ${}^1B_{2u} \longleftarrow {}^1A_{1g}$, clearly shows increase in intensity and the decrease in energy upon deprotonation of the species and increase in electronic delocalization: pH 2, the major species H_4C and H_3C^-, $\lambda_{max} = 293$ nm; pH 3.5, major species H_2C^{2-}, $\lambda_{max} = 295$ nm; pH 6, major species HC^{3-}, $\lambda_{max} = 300$ nm; pH 10, species C^{4-}, $\lambda_{max} = 315$ nm.

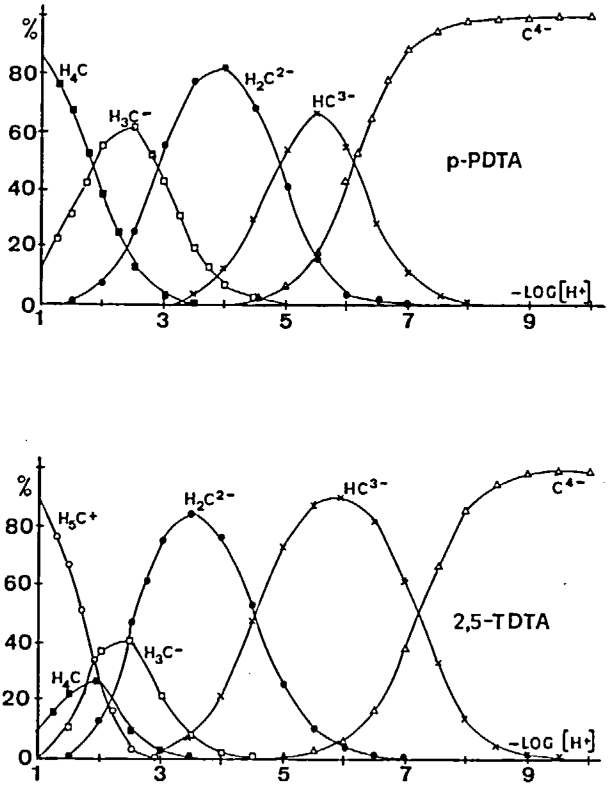


FIGURE 1 Species distribution as a function of $-\log[H^+]$: (a) *p*-PDTA; (b) 2,5-TDTA.

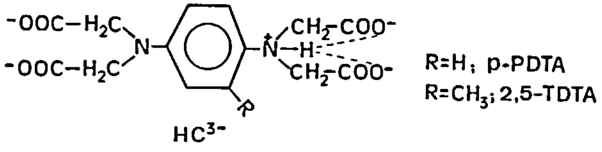


FIGURE 2 Structure proposed for the species HC^{3-}.

Stability constants of the complexes formed

The analysis of the experimental data for the metal-ligand system studied by the NERNST/LETA/GRAFICA version of the LETAGROP program allowed us to calculate β_{pqr} constants for the complex species formed, defined by means of equilibrium (*2*)

$$pH^+ + qCu^{2+} + rH_4C \rightleftharpoons [H_pCu_q(H_4C)_r]^{(p+2q)+} \qquad (2)$$

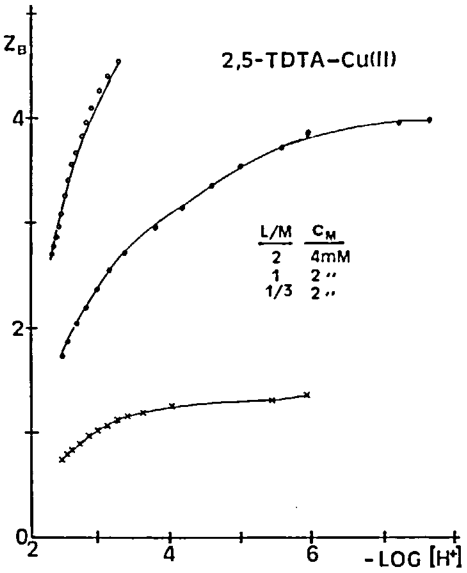


FIGURE 3 Z_B *vs* $-\log[H^+]$ curves for the 2,5-TDTA-Cu(II) system; full curves have been calculated using the β_{pqr} constants in Table II.

TABLE II

Stability constants for the complexes of 2,5-TDTA acid with Cu(II) (25°C, $I = 0.1$ M in KCl).

pqr	$-\text{Log}\ \beta_{pqr}$	Species	log K	log K (p-PDTA)[1,2]
−211		CuH_2C		4.69
−311	4.14 ± 0.05	$[CuHC]^-$	4.70	6.95
−411	8.82 ± 0.11	$[CuC]^{2-}$	7.23	8.16
−412	3.22 (>3.00)	$[Cu(H_2C)_2]^{2-}$	5.36	8.32
−512	≈0	$[Cu(H_2C)(HC)]^{3-}$		9.64
−612	11.30 (>10.28)	$[Cu(HC)_2]^{4-}$	6.38	10.14
−712	≈0	$[Cu(HC)C]^{5-}$		11.50
−321	≈0	$[Cu_2HC]^+$		8.94
−421	4.87 ± 0.04	Cu_2C	11.18	12.82
Equilibrium (*3*) $[CuC]^{2-} + Cu^{2+} \rightleftharpoons Cu_2C$			3.95	4.66

	Equilibrium	pKi	pKi(*p*-PDTA)[1,2]
(*4*)	$[CuHC]^- \rightleftharpoons [CuC]^{2-} + H^+$	4.68	4.90
(*5*)	$[Cu(H_2C)_2]^{2-} \rightleftharpoons [Cu(HC)_2]^{4-} + 2H^+$	8.08	7.92
(*6*)	$H_2C^{2-} + Cu^{2+} \rightleftharpoons [CuHC]^- + H^+$	0.15	2.12
(*7*)	$HC^{3-} + Cu^{2+} \rightleftharpoons [CuC]^{2-} + H^+$	0.02	2.05
(*8*)	$[CuHC]^- + Cu^{2+} \rightleftharpoons Cu_2C + H^+$	0.73	0.24

No. of titrations/No. of experimental points	7/143
Standard deviation [σ(Z)]	0.045
$-\text{Log}\ [H^+]$ range	2.29–8.74

The model that best fits the experimental results is that which corresponds to the complex species indicated in Table II. The validity of the same is proven in Fig. 3, where an excellent fit can be observed between the experimental Z_B *vs* $-\log[H^+]$ curves and those calculated from the values of β_{pqr} given in Table II. From the β_{pqr} constants, and taking into account the β_{pr} constants of the acid given in Table I, the stability constants, K, of the complex species formed can readily be calculated (Table II). Here, they are also contrasted with data for *p*-PDTA acid.[1,2]

The values of pKi ($= -\log$ Ki), corresponding to the ionization of the protonated complex species (equilibria (*4*) and (*5*), and equilibria (*6*), (*7*) and (*8*), readily obtained from Tables I and II, are also given in Table II. Values for *p*-PDTA acid[1,2] are also given in Table II.

The diagrams for the distribution of species of Cu(II) as a function of $-\log[H^+]$ were calculated from the values of β_{pr} given in Table I and those of β_{pqr} in Table II for 2,5-TDTA acid, and from the values of β_{pr} and β_{pqr} given in Ref. 1 for *p*-PDTA acid. They are plotted in Fig. 4 (ligand:metal ratio 2:1), Fig. 6 (ratio 1:1) and Fig. 7 (ratio 1:2) (C_M = 2mM).

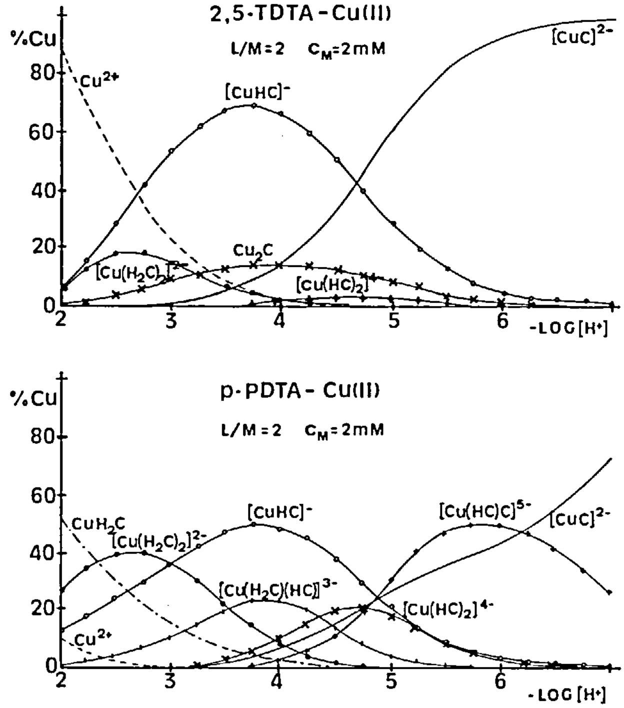
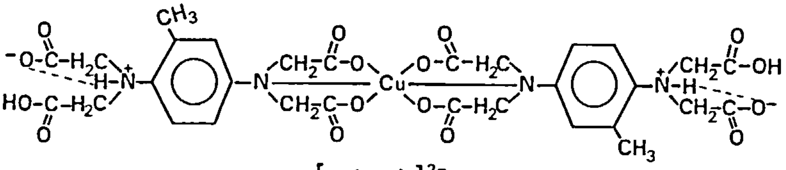


FIGURE 4 Species distribution as a function of $-\log[H^+]$ at the ligand:metal ratio 2:1: (a) 2,5-TDTA–Cu(II) system; (b) *p*-PDTA–Cu(II) system.

The values of log K (Table II) indicate the order of coordinating capacity *p*-PDTA > 2,5-TDTA. This order is valid for all the complex species, and is attributed to the repulsive steric effects of the methyl radical on the metallic cation. This decrease in the stability of the complex species of Cu(II) with 2,5-TDTA acid, with respect to *p*-PDTA acid, is more marked in the complex species with excess ligand, some of which, while stable for *p*-PDTA acid, are practically non-existent for 2,5-TDTA acid (Table II). Furthermore, the species present, $[Cu(H_2C)_2]^{2-}$ (Fig. 5) and $[Cu(HC)_2]^{4-}$, are found in small proportion, as can be observed in the diagrams of distribution of species (Fig. 4); it is seen that at pH 2.5 the species $[Cu(H_2C)_2]^{2-}$ is 18% abundant for 2.5-TDTA acid and 40% for *p*-PDTA acid. The respective percentages for the more unstable species $[Cu(HC)_2]^{4-}$ at pH 4.5 are 2% and 20%, respectively. Moreover, the presence of the species with excess of metal, Cu_2C, can be observed in Fig. 4a, while this species is (practically) not observed for *p*-PDTA acid (Fig. 4b), due to the much greater stability of the species with excess of ligand for this acid. This drastic decrease in the stability of these species must be attributed to the accumulated repulsive effects involving two CH_3 groups (Fig. 5).



$[Cu(H_2C)_2]^{2-}$

FIGURE 5 Structure proposed for the complex $[Cu(H_2C)_2]^{2-}$.

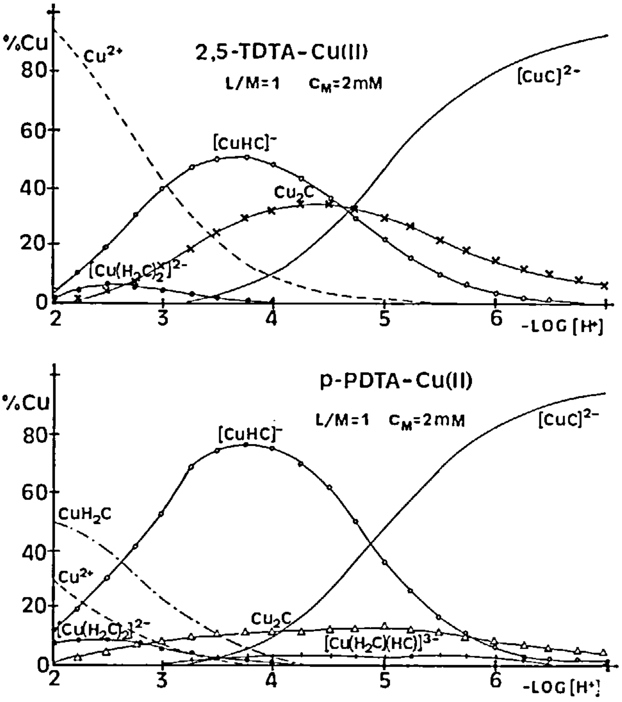


FIGURE 6 Species distribution as a function of $-\log[H^+]$ at the ligand:metal ratio 1:1: (a) 2,5-TDTA-Cu(II) system; (b) *p*-PDTA-Cu(II) system.

The decrease in stability of the complex species of Cu(II) with 2,5-TDTA acid, with respect to the corresponding species of *p*-PDTA acid, is smaller when only one CH_3 group brings repulsive effects to bear upon the complex species (complex $[CuHC]^-$, Fig. 6, 48% at pH 3.5 for 2,5-TDTA acid and 75% for *p*-PDTA acid; complex $[CuC]^{2-}$ (Fig. 6), at pH 6, 75% (2,5-TDTA) and 80% (*p*-PDTA); complex Cu_2C (Fig. 7), at pH 6, 70% (2,5-TDTA) and 85% (*p*-PDTA)).

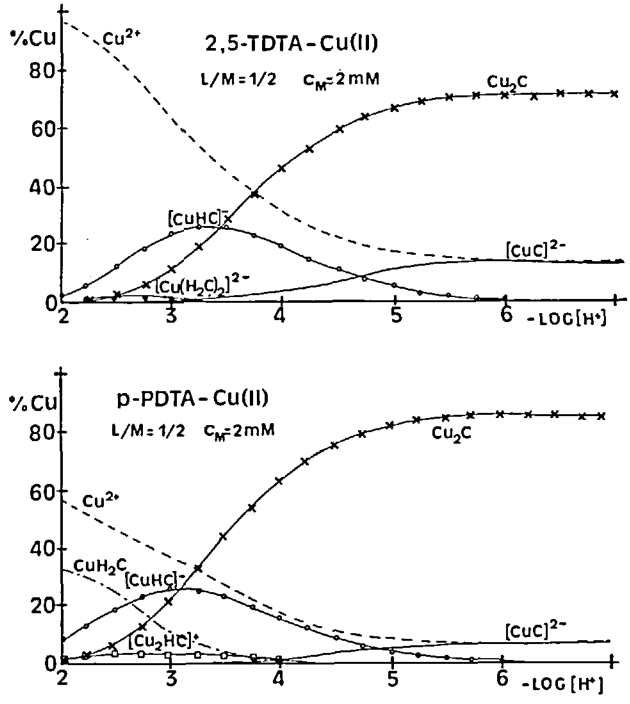


FIGURE 7 Species distribution as a function of $-\log[H^+]$ at the ligand:metal ratio 1:2: (a) 2,5-TDTA-Cu(II) system; (b) *p*-PDTA-Cu(II) system.

The values of pKi for the monoprotonated species $[CuHC]^-$ (equilibrium (*4*), Table II) are close to those of pK_3 of the ligand, indicating that this proton is fundamentally betainic; in the complex $[CuHC]^-$ the proton is bonded to one N atom and the Cu(II) ion to the other. The displacement of this proton by another Cu(II) ion to form the bimetallic species Cu_2C (equilibrium (*8*), Table II) represents a very strong acidity. This indicates the great stability of the species Cu_2C in which each Cu atom is bonded to an iminodiacetic group in a similar way to the complex Cu_2C for *p*-PDTA acid, as manifested by means of X-ray diffraction analysis of its structure.[13]

The electronic spectrum also reveals coordination of Cu(II) to the N atom; the energy and the intensity in particular of the band $^1B_{1u} \leftarrow {}^1A_{1g}$ is greatly affected by the electronic delocalization[9-12] of the electrons on the N atoms towards the system of π orbitals of the aromatic ring. A maximum decrease in intensity of this band at pH 6 can be observed, coinciding with the maximum stability of the species $[CuC]^{2-}$. The band $^1B_{2u} \leftarrow {}^1A_{1g}$ also undergoes an increase in energy upon complexation of

Cu(II). The maximum intensity for this band is at pH 6 since the excited singlet $^1B_{2u}$ term corresponds to an excited homopolar state, while the $^1B_{1u}$ term corresponds to an excited heteropolar state.[9-12]

In the visible spectrum, the complex $[CuC]^{2-}$, with a complexed N atom, gives rise to a band at 415 nm, which corresponds with the yellow colour of the complex. Cu(II) is relatively easy to reduce to Cu(I) such that many ligands give rise to ligand to metal charge transfer transitions. These ligands, as tetramethylcarboxylic acids derived from *para* or *meta*-phenylenediamines, exhibit $\sigma^* \longleftarrow \sigma$ transitions from the Cu–N bond to the empty x^2–y^2 orbital in a tetragonal or square planar complex.[3,9,14] The band at 415 nm is a $M \longleftarrow L$ charge transfer band. In the complex Cu_2C, where both N atoms are bonded to the Cu(II) ion, the electronic delocalization is smaller; the charge transfer band appears at ≈375 nm, accompanied by a much less intense band at ≈775 nm.[3,9,14]

ACKNOWLEDGMENTS

This work has been carried out under the Agreement of Scientific and Academic Cooperation signed in 1984 by the Faculty of Chemistry of the University of La Laguna (ULL) and the Faculty of Science of the Central University of Venezuela (UCV). We wish to thank the Computer Center of the Faculty of Science (UCV) for computer time at Burroughs 6700, as well as CONICIT (Caracas, Grant No. 51.78.31.S1–1228), CDCH (UCV, Grant No. C-03.12/83) and the Education Council of the Canary Islands Government (Grant No. 14/02.06.87) for financial support.

REFERENCES

1. A. Mederos, J.M. Felipe, F. Brito and K. Bazdikian, *J. Coord. Chem.*, **14**, 285 (1986).
2. A. Mederos, A. Benítez, A. Rancel, R. Guerra, F. Brito, K. Bazdikian and J. Bruzal, *J. Coord. Chem.*, **15**, 85 (1986).
3. B. Rodríguez Ríos and A. Mederos, *An. Quím.*, **65**, 557, 743 and 751 (1969).
4. B. Rodríguez Ríos and A. Mederos, *An. Quím.*, **64**, 983 (1968).
5. F. Brito, A. Mederos, P. Gili, S. Domínguez and P. Martín-Zarza, *J. Coord. Chem.*, **17**, 311 (1988).
6. F. Brito, A. Mederos, J.V. Herrera, S. Domínguez and M. Hernández-Padilla, *Polyhedron*, **7**, 1187 (1988).
7. R.N. Sylva and M.R. Davidson, *J. Chem. Soc., Dalton Trans.*, 232 (1979).
8. R.M. Smith and A.E. Martell, "Critical Stability Constants", Vol. 4, (Plenum Press, New York, 1976), p. 1.
9. A. Mederos, A. Rodríguez González and B. Rodríguez Ríos, *An. Quím.*, **69**, 601 (1973).
10. A. Mederos, F.G. Manrique, J.V. Herrera, M, Alvarez-Romero and J.M. Felipe, *An. Quím.*, **82B**, 133 (1986).
11. D.S. Schonland, "Molecular Symmetry", (van Nostrand, London, 1965).
12. D.C. Harris and M.D. Bertolucci, "Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy", (Oxford University Press, New York, 1978).
13. C. Ruiz-Pérez, M.L. Rodríguez, F.V. Rodríguez-Romero, A. Mederos, P. Gili and P. Martín-Zarza, *Acta Cryst.*, in press.
14. A.B.P. Lever, "Inorganic Electronic Spectroscopy", 2nd Edn., (Elsevier, Amsterdam, 1984).