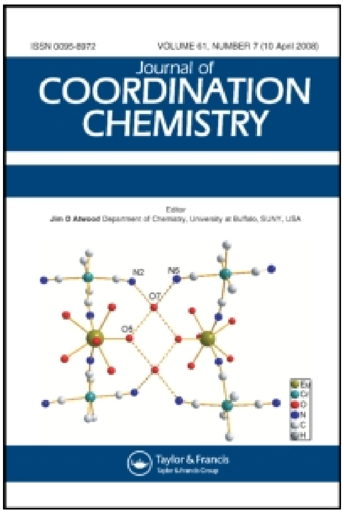

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPLEX SPECIES IN AQUEOUS SOLUTION OF *META*-PHENYLENEDIAMINE-*N,N,N',N'*-TETRAACETIC AND *PARA*-PHENYLENEDIAMINE-*N,N,N',N'*-TETRAACETIC ACIDS IN THE PRESENCE OF COPPER(II)

A. Mederos[a]; J. M. Felipe[a]; F. Brito[b]; K. Bazdikian[b]
[a] Departamento de Quimica Inorgánica, Facultad de Quimica, Universidad de La Laguna, Canary Islands, Spain [b] Laboratorio de Equilibrios en Solución, Escuela de Quimica, Facultad de Ciencias, Universidad Central de Venezuela, Caracas

To cite this Article Mederos, A. , Felipe, J. M. , Brito, F. and Bazdikian, K.(1986) 'COMPLEX SPECIES IN AQUEOUS SOLUTION OF *META*-PHENYLENEDIAMINE-*N,N,N',N'*-TETRAACETIC AND *PARA*-PHENYLENEDIAMINE-*N,N,N',N'*-TETRAACETIC ACIDS IN THE PRESENCE OF COPPER(II)', Journal of Coordination Chemistry, 14: 4, 285 — 291

To link to this Article: DOI: 10.1080/00958978608075846

URL: http://dx.doi.org/10.1080/00958978608075846

J. Coord. Chem. 1986, Vol. 14. p.285–291
0095-8972/86/1404-0285 $18.50/0

COMPLEX SPECIES IN AQUEOUS SOLUTION OF *META*-PHENYLENEDIAMINE-*N,N,N′,N′*-TETRAACETIC AND *PARA*-PHENYLENEDIAMINE-*N,N,N′,N′*-TETRAACETIC ACIDS IN THE PRESENCE OF COPPER(II)

A MEDEROS† and J.M. FELIPE

Departamento de Quimica Inorgánica, Facultad de Quimica, Universidad de La Laguna, Canary Islands, Spain

F. BRITO and K. BAZDIKIAN

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

(Received August 1, 1985)

The special conformation of the potentially hexadentate *m*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid (*m*-PDTA) and *p*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid (*p*-PDTA) ligands, led to the formation of a high number of complex species with Cu(II) in aqueous solution, on varying the ligand/metal relationships. The calculations indicate that the model that best fits the experimental results is that which takes into account the existence of ten complex species for the system *m*-PDTA/Cu(II) and nine for *p*-PDTA/Cu(II).

Keywords: Stabilities, copper, hexadentates, EDTA-type ligands, complexes

INTRODUCTION

The preparation of coordinating agents derived from aromatic diamines is of special interest, since the use of nitrogen atoms for coordination to a single cation is directly related to their situation in *ortho*, *meta* or *para* positions. Thus, in the case of diaminepolycarboxylic acids, the derivatives of *meta* or *para*-phenylenediamines can only coordinate a single atom of nitrogen to any one cation. These ligands can therefore coordinate in two spheres, as has been proved in the preparation of bimetallic species in the solid state for the *m*-PDTA and *p*-PDTA acids[1], of the M_2C type (ligands, H_4C), as well as the possible formation of species with excess ligand, since each iminodiacetic group of the ligand is insufficient to coordinatively saturate the central ion, as confirmed by us when studying 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 = *ortho*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid)[3], confirming our studies in aqueous solution of the coordinating capacity of the *o*-PDTA acid and 3,4-TDTA (3,4-TDTA = 3,4-toluenediamine-*N,N,N′,N′*-tetraacetic acid) with Cu(II)[4] and Be(II).[5] For the above-mentioned reasons, a thorough potentiometric study in aqueous solution of the systems *m*-PDTA/Cu(II) and *p*-PDTA/Cu(II) should take into account not only the complexes formed in the ratio 1/1, and their possible dimerization to form

---

† Author for correspondence.

complexes in the ratio 2/2, evidence of which has been found for the *m*-PDTA acid in solid state with Ni(II), Co(II) and Cu(II),[6] but should also consider the existence of complex species, both with excess of ligand and excess of metal. This was the purpose of the present work since previous potentiometric,[7–9] polarographic[10] and spectrophotometric[11] studies of these systems are limited since they do not take into account all the above-mentioned considerations.

EXPERIMENTAL

The *m*-PDTA acid was prepared according to the Blasius and Olbrich method.[12] The *p*-PDTA acid was prepared in a similar manner, first precipitating and purifying the white disodium salt and then acidifying its concentrated aqueous solution with HCl (25%) to pH 1, to afford a white precipitate of *p*-PDTA acid. Precautions were taken to maintain an inert atmosphere (argon) and prevent the access of light during the preparation and preservation of both acids and during the study of their solutions, since they are photosensitive and oxidize readily.

The potentiometric measurements were carried out in aqueous solution at ionic strength 0.1 M in KCl and 25.00 ± 0.05. A Radiometer Type PHM-64 potentiometer was used, with a Radiometer G 202 B glass electrode and a K 401 calomel electrode. Concentrations of ligand of 0.5, 1.0 and 1.5 mM were studied, varying the concentration of Cu(II) (in the form of chloride) in the ligand/metal ratios 1/1, 1/2 and 2/1. Larger ratios were not used to prevent the possible formation of higher polymeric complex species.[8,9] CO_2-free NaOH 0.1 M was used as the titrant. The calculation and refinement of both the constants of protonation of the ligands and of the stability constants of the complex species formed was carried out by digital computation by means of the NERNST/LETA/GRAFICA version[13] of LETAGROP.[14] It was found that under the experimental conditions used hydrolysis of Cu(II) is negligible.

RESULTS

Ionization Constants of the Acids

The pK_i of the corresponding ionization constants presented in Table I were readily obtained from the values of $-\log \beta_{pq}$, obtained and refined by applying the LETAGROP program to the potentiometric experimental data, and which correspond to the equilibria (*1*).

$$-pH^+ + H_4C \rightleftharpoons H_{4-p}C^{p-} \qquad (1)$$

TABLE I
Ionization Constants of *m*-PDTA and *p*-PDTA Acids (25; $\mu = 0.1$ M in KCl)

pq	$-\log \beta_{pq}$		Species	pK_i	
	m-PDTA	*p*-PDTA		*m*-PDTA	*p*-PDTA
-11	2.107 ± 0.016	1.830 ± 0.227	H_4C/H_3C^-	2.11	1.83
-21	4.895 ± 0.001	4.717 ± 0.193	H_3C^-/H_2C^{2-}	2.79	2.87
-31	9.894 ± 0.012	9.588 ± 0.199	H_2C^{2-}/HC^{3-}	5.00	4.87
-41	15.641 ± 0.010	15.699 ± 0.199	HC^{3-}/C^{4-}	5.75	6.11

Dispersion, $\sigma(Z_c) = 0.006$ (*m*-PDTA), $\sigma(Z_c) = 0.010$ (*p*-PDTA)

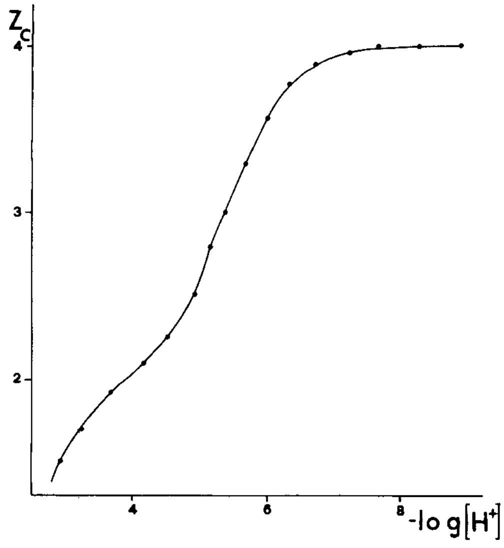

FIGURE 1 $Z_C(-\log[H^+])$ curves for *m*-PDTA acid. Dotted line, experimental curve. Unbroken line, calculated curve.

The validity of these results can be seen in Fig. 1 where the $Z_c(-\log[H^+])$ curves for the *m*-PDTA acid are plotted, Z_c being the average number of dissociated protons for the total ligand concentration, H_4C, with an excellent agreement between the calculated curves and those obtained experimentally. The values of the pK_i for both acids are in good accordance with the literature date.[15] 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.[11]

TABLE II

Stability Constants of *m*-PDTA and *p*-PDTA Acids with Cu(II) at 25°; $\mu = 0.1$ M in KCl.

pqr	$-\log \beta_{pqr}$ *m*-PDTA	 *p*-PDTA	Species	log K *m*-PDTA	 *p*-PDTA
-211	0.422 ± 0.020	0.024 ± 0.078	CuH_2C	4.47	4.69
-311	3.243 ± 0.020	2.642 ± 0.062	$CuHC^-$	6.65	6.95
-411	7.424 ± 0.025	7.538 ± 0.080	CuC^{2-}	8.22	8.16
-412	2.166 ± 0.148	1.108 ± 0.176	$Cu(H_2C)_2^{2-}$	7.62	8.32
-512	5.135 ± 0.072	4.666 ± 0.203	$Cu(H_2C)(HC)^{3-}$	9.65	9.64
-612	9.629 ± 0.207	9.033 ± 0.260	$Cu(HC)_2^{4-}$	10.16	10.14
-712	14.527 ± 0.205	13.786 ± 0.111	$Cu(HC)C^{5-}$	10.81	11.50
-812	20.636 ± 0.181		CuC_2^{6-}	10.65	
-321	1.072	0.651	Cu_2HC^+	2.17	1.99
-421	3.572 ± 0.055	2.880 ± 0.047	Cu_2C	3.67	4.66

Dispersion, $\sigma(Z) = 0.034$ (*m*-PDTA), $\sigma(Z) = 0.035$ (*p*-PDTA)

Stability Constants of the Complexes Formed

In a similar manner, and taking into account the pK_i, the stability constants K given in Table II of the complex chemical species present for each ligand were readily obtained from the values of $-\log \beta_{pqr}$ corresponding to 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, is that which corresponds to the complex species indicated in the above-mentioned Table. The validity of the same can be observed in Figures 2 and 3, where the $Z_B(-\log[H^+])$ curves are plotted for the acids *m*-PDTA and *p*-PDTA, respectively, and where Z_B is the average number of dissociated protons with respect to the total concentration of metal. A good agreement is observed between the experimental curves and the calculated ones.

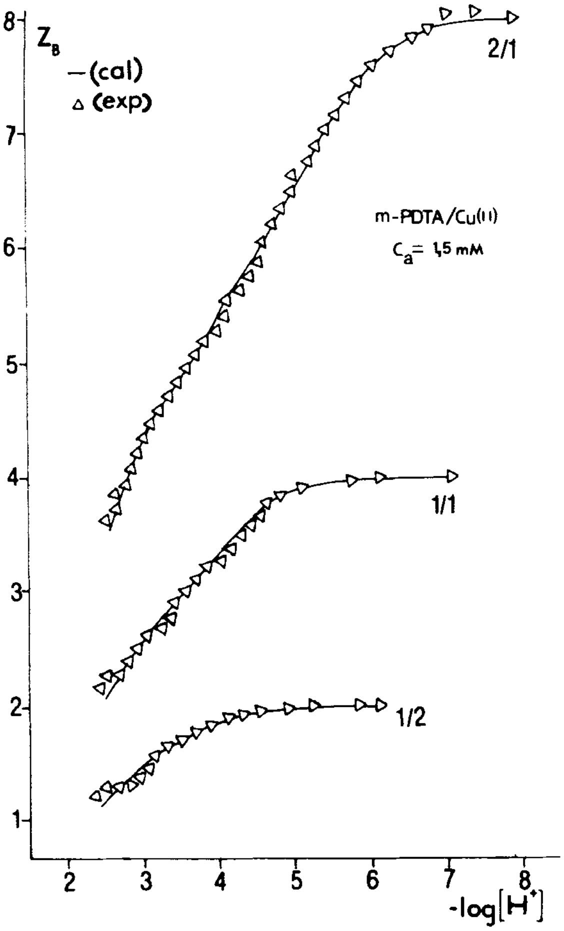

FIGURE 2 $Z_B(-\log[H^+])$ curves of the system *m*-PDTA-Cu(II). Triangles, experimental curve. Unbroken line, calculated curve.

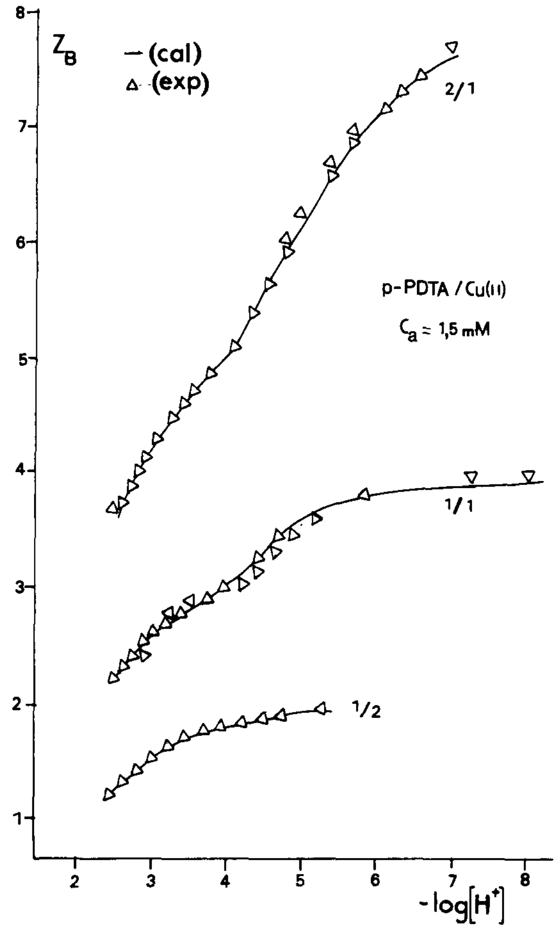

FIGURE 3 $Z_B(-\log[H^+])$ curves of the system *p*-PDTA-Cu(II). Triangles, experimental curve. Unbroken line, calculated curve.

The values of pK_i corresponding to the ionization of the protonation complex species, readily obtained from Tables I and II, are given in Table III.

TABLE III

Ionization Constants of the Protonated Complex Species (25°; $\mu = 0.1$ M in KCl).

Species	pK_i *m*-PDTA	pK_i *p*-PDTA
$CuH_2C/CuHC^-$	2.82	2.61
$CuHC^-/CuC^{2-}$	4.18	4.90
$Cu(H_2C)_2^{2-}/Cu(H_2C)(HC)^{3-}$	2.97	3.55
$Cu(H_2C)(HC)^{3-}/Cu(HC)_2^{4-}$	4.49	4.37
$Cu(HC)_2^{4}/Cu(HC)C^{5-}$	5.10	4.75
$Cu(HC)C^{5-}/CuC_2^{6-}$	5.91	
Cu_2HC^+/Cu_2C	4.39	3.44

DISCUSSION

The results given above confirm the theoretical predictions, according to which the type of complex species in aqueous solution for diaminepolycarboxylic acids derived from aromatic diamines, in the presence of the Cu(II) ion, is a function of the different situation of the iminodiacetic groups on the ring. Thus, while in the *ortho* position (the systems *o*-PDTA/Cu(II) and 3,4-TDTA/Cu(II) were studied by us[4]), only significant amounts of the monoprotonated $CuHC^-$ and no protonated CuC^{2-} complexes are formed, in a similar manner to EDTA, since the proximity of the nitrogen atoms in the *ortho* position favours the simultaneous coordination of both iminodiacetic groups to one and the same metallic cation. This cation is allowed to toally fulfil its coordination requirements. The *m*-PDTA and *p*-PDTA acids form, as well as the expected complexes in the ratio 1/1 and bi-metallic species, complexes with excess of ligand, detected for the first time in this work.

The formation of the complexes CuH_2C, $CuHC^-$ and CuC^{2-}, which were indeed found, is to be expected for complexes in the ratio 1/1, in which the *m*-PDTA and *p*-PDTA acids only use one of the iminodiacetic groups for coordination to the metallic atom, the other iminodiacetic group becoming protonated. The stability constants (Table II) increase on passing from the CuH_2C to the CuC^{2-} complex, which can be ascribed to a shift of the electronic density towards the nitrogen atom directly bonded to the metallic atom, as a consequence of the successive ionizations of a basically carboxylic proton and of another fundamentally betainic proton. (Compare values in Table III with those in Table I). The complexes CuH_2C and $CuHC^-$ are slightly more stable for *p*-PDTA acid, whereas the stability of the non-protonated complex, CuC^{2-}, is practically the same for both acids. The calculations indicate that, at least at the concentrations studied from 0.5 mM to 1.5 mM, the complexes in the ratio 1/1 are not dimerized to the ratio 2/2, as postulated for *m*-PDTA acid.[6]

As could be expected from the presence of two coordination spheres, each of which corresponds to one of the iminodiacetic groups, these ligands form the bimetallic species, Cu_2C, already detected in previous work for *m*-PDTA acid[7,9] and for *p*-PDTA acid,[8] although its stability constants could not be correctly established. It is interesting to note that the monoprotonated species, Cu_2HC^+, is also formed, probably protonated over one of the nitrogen atoms, in which case one of the Cu(II) ions would be bonded to the carboxylate groups of an iminodiacetic group, thus explaining the lesser stability of this species. The possible formation of protonated complex species with excess of metal was assumed in an earlier work when studying the curve with an excess of metallic cation of 15/1.[8]

The formation of complexes with excess ligand, proven for *m*-PDTA *and p*-PDTA acids for the first time in this work, is not surprising if it is remembered that only a terdentate iminodiacetic group of a ligand can be bonded to one metallic cation. There is therefore a tendency for two iminodiacetic groups of different ligands to bond (Figure 4).

Both uncoordinated iminodiacetic groups can be protonated as observed in the species $Cu(H_2C)_2^{2-}$. Two of the protons of this species are basically carboxylic and another two are fundamentally betainic, as can be deduced from the values of the ionization constants presented in Table III and compared with those in Table I.

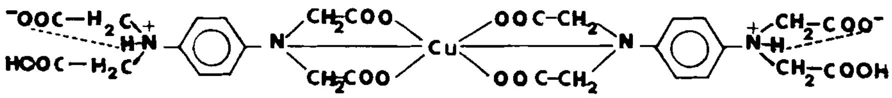

FIGURE 4 $Cu(H_2C)_2^{2-}$ species for *p*-PDTA acid.

The different degrees of protonation correspond to the different species found, the stability constants of which are given in Table II. The stability of the species increases as expected, as the number of protons decreases, to the monoprotonated species $Cu(HC)C^{5-}$, the stability being practically identical for both ligands. Surprisingly, the species CuC_2^{6-}, no longer practically detected for the *p*-PDTA acid, is less stable, which may be due to the great stability of the species CuC^{2-}, since the equilibrium (*3*)

$$CuC^{6-} \rightleftharpoons CuC^{2-} + C^{4-} \tag{3}$$

is completely shifted to the right in the case of *p*-PDTA acid.

REFERENCES

1. E. Uhlig and D. Herrmann, *Z. Anorg. allg. Chem.*, **360,** 158 (1968)
2. A. Mederos, S. Dominguez, M. Hernàndez-Padilla, F. Brito and E. Chinea, to be published. Communication to the Congreso Iberoamericano de Ciencias Quimicas, Lima, Peru.(1983). Book of Abstracts.
3. E.F.K. McCandlish, T.K. Michael, J.A. Neal, E.C. Lingafelter and N.J. Rose, *Inorg. Chem.*, **17,** 1383 (1978).
4. A. Mederos, J.M. Felipe, F. Brito and K. Bazdikian, to be published.
5. A. Mederos, J.M. Felipe, M. Hernàndez-Padilla, F. Brito, E. Chinea and K. Bazdikian, to be published.
6. S. Gonzàlez Carcia and F.J. Sànchez Santos, An. Quim., **72,** 148, 153 (1976) and **77, B,** 175 (1981).
7. E. Uhlig and D. Herrmann, *A. Anorg. allg. Chem.*, **359,** 135 (1968).
8. B. Rodriguez Rios and A. Mederos, *An. Quim.*, **65, B,** 649 (1969).
9. A. Mederos, A. Rodriguez Gonzàez and B. Rodriguez Rios, *An. Quim.*, **66,** 531 (1970).
10. S.K. Chu and C.F. Chen, *J. Chinese Chem. Soc. (Taiwan)*, **16,** 68 (1969).
11. A. Mederos, A. Rodriguez Gonzàlez and B. Rodriguez Rios, *An. Quim.*, **69,** 601 and 731 (1973).
12. E. Blasius and G. Olbrich, *Z. Analyt. Chem.*, **151,** 81 (1956).
13. F. Brito and J.M. Goncalves, Project Num. 51.78.31-S1-1228, CONICIT (1981), Caracas, Venezuela.
14. R. Arnek, L.G. Sillèn and O. Wahlberg, *Arkiv Kemi*, **31,** 353 (1969).
15. A.E. Martell and R.M. Smith, *Critical Stability Constants. Vol. 1: AminoAcids.* Plenum Press, New York (1974), pp. 362-364.