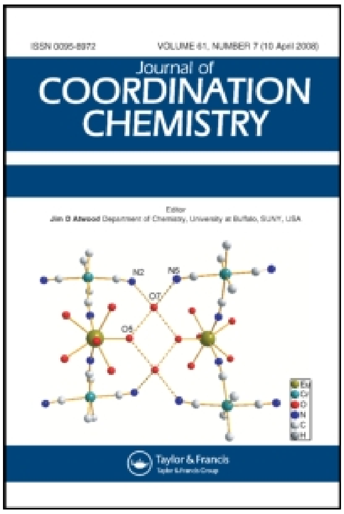

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Dimer Species in Aqueous Solutions of 2,6-Toluenediamine-*N,N,N',N'*-Tetraacetic Acid with Copper(II), Nickel(II), Cobalt(II) and Zinc(II)

S. Dominguez[a]; A. Rancel[a]; J. V. Herrera[a]; A. Mederos[a]; F. Brito[b]
[a] Departamento de Quimica Inorganica, Universidad de La Laguna, Tenerife, Canary Islands, Spain [b] Laboratorio de Equilibrios en Solution, Escuela de Quimica. Facultad de Ciencias. Universidad Central de Venezuela, Caracas, Venezuela

To cite this Article Dominguez, S. , Rancel, A. , Herrera, J. V. , Mederos, A. and Brito, F.(1992) 'Dimer Species in Aqueous Solutions of 2,6-Toluenediamine-*N,N,N',N'*-Tetraacetic Acid with Copper(II), Nickel(II), Cobalt(II) and Zinc(II)', Journal of Coordination Chemistry, 25: 4, 271 — 282

To link to this Article: DOI: 10.1080/00958979209409201

URL: http://dx.doi.org/10.1080/00958979209409201

J. Coord. Chem. 1992, Vol. 25, pp. 271–282
Reprints available directly from the publisher
Photocopying permitted by license only

DIMER SPECIES IN AQUEOUS SOLUTIONS OF 2,6-TOLUENEDIAMINE-*N*,*N*,*N'*,*N'*-TETRAACETIC ACID WITH COPPER(II), NICKEL(II), COBALT(II) and ZINC(II)

S. DOMINGUEZ, A. RANCEL, J. V. HERRERA, A. MEDEROS*

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

and F. BRITO

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

(Received July 15, 1991)

The complex species formed in aqueous solution between 2,6-toluenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (2,6-TDTA) and Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Mn(II), respectively, were studied at 25°C and ionic strength 0.1 M in KCl. The application of the least-squares computer program SUPERQUAD to the experimental potentiometric data indicates that, upon varying the ligand : metal relationships and concentrations, the following complex species are formed (ligand, H_4L): Cu(II) (CuH_2L, $[CuHL]^-$, $[CuL]^{2-}$, $[Cu_2H_2L]^{2+}$, Cu_2L, $[Cu_2HL_2]^{3-}$ and $[Cu_2L_2]^{4-}$); Ni(II) (NiH_2L, $[NiHL]^-$, $[NiL]^{2-}$, $[Ni_2HL]^+$, $[Ni_2HL_2]^{3-}$ and $[Ni_2L_2]^{4-}$); Co(II) ($[CoHL]^-$, $[CoL]^{2-}$, $[Co_2H_2L]^{2+}$, $[Co_2HL]^+$, $[Co_2HL_2]^{3-}$ and $[Co_2L_2]^{4-}$); Zn(II) (ZnH_2L, $[ZnHL]^-$, $[ZnL]^{2-}$, $[Zn_2H_2L]^{2+}$, $[Zn_2HL_2]^{3-}$ and $[Zn_2L_2]^{4-}$); Cd(II) (CdH_2L, $[CdHL]^-$, $[CdL]^{2-}$ and $[CdHL_2]^{5-}$; and Mn(II) (MnH_2L, $[MnHL]^-$ and $[MnL]^{2-}$). The dimer species $[M_2L_2]^{4-}$ has been identified for the first time in potentiometric studies in aqueous solution. Compared with *m*-PDTA acid, the order of coordinating ability 2,6-TDTA ≪ *m*-PDTA (*m*-PDTA = *meta*-phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid) is attributed to the repulsive steric effects of the methyl group.

Keywords: Copper, nickel, cobalt, zinc, 2,6-toluenediamine, multidentates, dimerization, stability constants

INTRODUCTION

In the case of diaminetetramethylenecarboxylic acids derived from *m*-phenylenediamines, the special conformation of the ligand with the nitrogen atoms in *meta* positions on the aromatic ring facilitates the formation of dimer complexes since the ligands may act as a bridge. This has been proven in the case of *m*-phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (*m*-PDTA) by means of studies in aqueous solution with Co(II),[1] Ni(II)[2] and Cu(II),[3] that confirm the presence of dimer species $[M_2L_2]^{4-}$ (ligand, H_4L). These species have also been found for pyridine-2,6-diamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (2,6-PyDTA) with Ni(II).[3] After studying the conditions for the formation of the dimer species $[M_2L_2]^{4-}$ in aqueous solution, single crystals of the complexes $Na_4[Cu_2(m\text{-PDTA})_2]\cdot 18H_2O$, $Na_4[Co_2(m\text{-PDTA})_2]\cdot 10H_2O$ and

---

* Author for correspondence.

$Na_4[Ni_2(2,6\text{-PyDTA})_2]\cdot 8H_2O$, respectively, were obtained, and their structures were determined[3] by X-ray diffraction analysis.

The presence of a methyl radical as substituent on the aromatic ring produces electrondonor inductive effects favourable to coordination, and unfavourable steric repulsion effects. The predominance of one or the other factor depends on the position of the methyl group with regard to the nitrogen atoms.

For 2,4-toluenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (2,4-TDTA), studies in aqueous solution also indicate the presence of the dimer species $[M_2L_2]^{4-}$ with Co(II), Ni(II), Cu(II) and Zn(II), and single crystals of the complexes $Na_4[Ni_2(2,4\text{-TDTA})_2]\cdot 15H_2O$ and $Na_4[Zn_2(2,4\text{-TDTA})_2]\cdot 15H_2O$ were obtained, their structures being determined[4] by X-ray diffraction analysis. The order of coordination ability *m*-PDTA > 2,4-TDTA is attributed to the repulsive steric effects of the methyl radical on the metallic cation.

In particular, the presence of a methyl radical as substituent on the aromatic ring between both nitrogen atoms produces greater repulsive effects.[5] In the present work we studied the possible presence of the dimer complex species $[M_2L_2]^{4-}$ in aqueous solution for 2,6-toluenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (2,6-TDTA) with Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Mn(II). Previous studies of the Cu(II)–2,6-TDTA system[5] did not take into account the possible presence of these species.

EXPERIMENTAL

2,6-TDTA acid was prepared according to the method of Mederos *et al.*[6] Precautions were taken to maintain an inert atmosphere (argon) and 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.

Potentiometry

The potentiometric titrations were carried out in aqueous solution at ionic strength 0.1 M in KCl and at 25 ± 0.05°C, using a Radiometer Type PHM-84 potentiometer, a Radiometer G 202 B glass electrode and a K 401 calomel electrode. The cell constants were determined according to the method of Bidermann and Sillén.[7] It was found that $pK_w = 13.74$, in excellent agreement with reported data.[8] A carbonate-free sodium hydroxide solution was prepared according to the method of Sillén[9] and standardized against potassium hydrogenphthalate. The metal solutions (in the form of the chloride) were standardized by routine methods. Potassium chloride was prepared by recrystallization of KCl. The compounds HCl, NaOH, KCl, $CuCl_2$, $NiCl_2$, $CoCl_2$, $ZnCl_2$, $CdCl_2$ and $MnCl_2$ were of analytical grade from Merck.

Measurements were taken of the ligand in the presence of metallic cation at the following ligand : metal ratios and concentrations: Cu(II), ratio 1 : 1 ($C_M = 0.5$, 1, 1.5, 6 and 10 mM), ratio 2 : 1 ($C_M = 0.25$ and 0.5 mM) and ratio 1 : 2 ($C_M = 1$, 2 and 3 mM); Ni(II), ratio 1 : 1 ($C_M = 0.5$, 1, 3 and 10 mM), and ratios 2 : 1 and 1 : 2 ($C_M =$ 0.5, 1 and 3 mM); Co(II), ratio 1 : 1 ($C_M = 0.5$, 1, 6 and 10 mM), ratio 2 : 1 ($C_M =$ 0.5 mM) and ratio 1 : 2 ($C_M = 0.6$ and 1 mM); Zn(II), ratio 1 : 1 ($C_M = 0.5$, 1, 1.5, 6 and 10 mM), ratio 3 : 1 ($C_M = 1$ mM) and ratio 1 : 3 ($C_M = 3$ mM); Cd(II), ratio 1 : 1 ($C_M = 0.5$, 1.2 and 1.5 mM), ratio 3 : 1 ($C_M = 1$ mM) and ratio 1 : 3 ($C_M = 3$ mM); and Mn(II), ratio 1 : 1 ($C_M = 0.5$, 1 and 1.5 mM), ratio 2 : 1 ($C_M = 0.5$ mM) and ratio 1 : 2 ($C_M = 2$ mM), respectively.

The experimental potentiometric data were analysed by means of the SUPERQUAD program.[10] It was found that, under the experimental conditions used, hydrolysis of the metallic cations was negligible. The ionization constants of 2,6-TDTA acid were previously obtained under the same experimental conditions.[5,6]

Conductimetry

The conductimetric titrations were carried out in an inert argon atmosphere, at 25°C, using a Digitalmeter Digi 610. Ionic strength was not adjusted. Measurements were taken of 2,6-TDTA alone and of 2,6-TDTA in the presence of Cu(II); Ni(II), Co(II), Zn(II), Cd(II) and Mn(II), respectively, at the ligand : metal ratio 1:1 and concentration C_L = 1 mM. NaOH 0.1 M was used as titration agent.

RESULTS AND DISCUSSION

The conductimetric titrations (Figure 1) show that 2,6-TDTA acid is a tetrabasic acid. A different behaviour is observed (ratio 1:1; C_M = 1 mM) for Cu(II), which complexes more strongly than the other cations whose behaviour is quite similar. The shape of the conductimetric curves is in agreement with the values of logK and pKi given in Table I and which have been obtained from the potentiometric titrations.

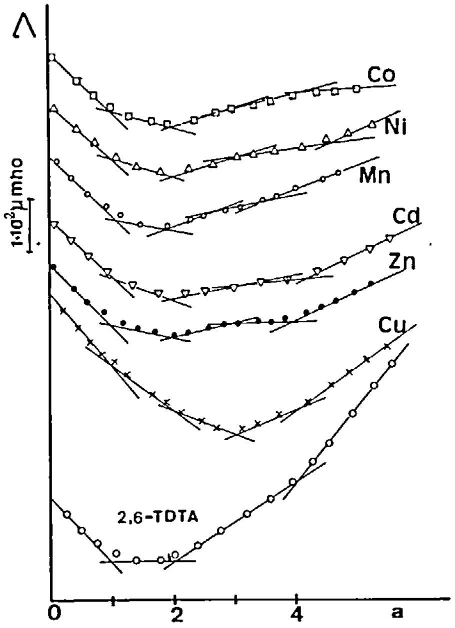

FIGURE 1 Conductimetric curves of free acid 2,6-TDTA and in the presence of different divalent cations in the ligand : metal ratio 1 : 1. C_M and C_L = 1 mM; conductivities, Λ, *vs* values of *a* (mols of NaOH/mol of acid).

TABLE I

Formation constants (log β_{pqr}) for 2,6-TDTA acid with Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Mn(II); 25°C; I = 0.1 M in KCl, and equilibrium constants.

pqr	Species	Cu(II)	Ni(II)	Co(II)	Zn(II)	Cd(II)	Mn(II)
211	$[MH_2L]$	14.06 ± 0.01	12.26 ± 0.03		12.68 ± 0.03	12.82 ± 0.06	13.44 ± 0.02
111	$[MHL]^-$	11.05 ± 0.01	8.33 ± 0.05	8.24 ± 0.04	8.98 ± 0.01	9.03 ± 0.02	9.15 ± 0.02
011	$[ML]^{2-}$	6.30 ± 0.04	2.73 ± 0.05^{a}	2.27 ± 0.04^{b}	3.28 ± 0.04	3.19 ± 0.03	3.16 ± 0.03
221	$[M_2H_2L]^{2+}$	16.10 ± 0.05		14.82 ± 0.01	14.43 ± 0.14		
121	$[M_2HL]^+$		10.64 ± 0.07	11.22 ± 0.01			
021	$[M_2L]$	9.69 ± 0.04					
112	$[MHL_2]^{5-}$					11.91 ± 0.11	
122	$[M_2HL_2]^{3-}$	19.50 ± 0.07	14.29 ± 0.03	14.61 ± 0.01	15.02 ± 0.03		
022	$[M_2L_2]^{4-}$	14.66 ± 0.10	8.77 ± 0.02	8.92 ± 0.01	9.79 ± 0.03		

	Equilibrium (log K values)	Cu(II)		Ni(II)		Co(II)		Zn(II)	Cd(II)	Mn(II)
(2)	$M^{2+} + H_2L^{2-}/[MH_2L]$	3.37	4.47^{c}	1.57	1.72^{d}		2.06^{e}	1.99	2.13	2.75
(3)	$M^{2+} + HL^{3-}/[MHL]^-$	4.92	6.65	2.19	3.98	2.10	3.33	2.84	2.90	3.01
(4)	$M^{2+} + L^{4-}/[ML]^{2-}$	6.30	8.28	2.73	5.26	2.27	5.02	3.28	3.19	3.16
(5)	$2M^{2+} + H_2L^{2-}/[M_2H_2L]^{2+}$	5.41				4.13		3.74		
(6)	$2M^{2+} + HL^{3-}/[M_2HL]^+$			4.50		5.08				
(7)	$2M^{2+} + L^{4-}/[M_2L]$	9.69								
(8)	$M^{2+} + HL^{3-} + L^{4-}/[MHL_2]^{5-}$								5.77	
(9)	$2M^{2+} + HL^{3-} + L^{4-}/[M_2HL_2]^{3-}$	13.36		8.15		8.47		8.89		
(10)	$2M^{2+} + 2L^{4-}/[M_2L_2]^{4-}$	14.66	17.92	8.77	14.38	8.92	12.93	9.79		
(11)	$M^{2+} + [MH_2L]/[M_2H_2L]^{2+}$	2.04						1.75		
(12)	$M^{2+} + [MHL]^-/[M_2HL]^+$			2.31		2.98				
(13)	$M^{2+} + [ML]^{2-}/[M_2L]$	3.39								
(14)	$[MHL]^- + L^{4-}/[MHL_2]^{5-}$								2.88	
(15)	$[MHL]^- + [ML]^{2-}/[M_2HL_2]^{3-}$	2.15		3.23		4.30		2.76		
(16)	$2[ML]^{2-}/[M_2L_2]^{4-}$	2.06	1.36	3.31	3.86	4.38	2.89	3.23		
(17)	$M^{2+} + H_2L^{2-}/[MHL]^- + H^+$	−0.36	−1.65^{c}	2.37	1.02^{d}	2.46	1.67^{e}	1.71	1.66	1.55
(18)	$[MH_2L]/[MHL]^- + H^+$	3.01	2.82	3.94	2.73		3.73	3.70	3.79	4.30

(*19*) $[MHL]^-/[ML]^{2-} + H^+$	4.76	4.18	5.59	4.47	5.97	4.06	5.70	5.85	5.99
(*20*) $2[MHL]^-/[M_2L_2]^{4-} + 2H^+$	7.45	7.00	7.88	5.08	7.55	5.23	8.17		
(*21*) $M^{2+} + H_2L^{2-}/[ML]^{2-} + 2H^+$	4.40	2.47	7.96	5.49	8.43	5.73	7.41	7.50	7.54
(*22*) $2M^{2+} + 2H_2L^{2-}/[M_2L_2]^{4-} + 4H^+$	6.73	3.58	12.62	7.12	12.46	8.57	11.59		
Number of titrations	10		10		7		7	5	5
Number of experimental points	255		174		176		220	195	189
Sigma	1.031		0.597		0.246		0.549	0.708	0.651
$-\log[H^+]$ range	2.1–6.9		2.5–6.2		2.4–6.6		2.7–6.3	2.8–8.4	2.8–8.9

[a] Obtained from $C_M = 0.5$ and 1 mM, ratios 2 : 1, 1 : 1 and 1 : 2; (six titrations). [b] Obtained from $C_M = 0.5$, 1 and 3 mM (ratio 1 : 1), $C_M = 0.5$ and 1 mM (ratio 2 : 1) and $C_M = 0.6$ and 1 mM (ratio 1 : 2); seven titrations. [c] For *m*-PDTA acid with Cu(II), Ref. 3. [d] For *m*-PDTA acid with Ni(II), Ref. 2. [e] For *m*-PDTA acid with Co(II), Ref. 1. [f] For 2,6-TDTA acid, pK_i: $H_5L^+/H_4L + H^+$, 1.81; $H_4L/H_3L^- + H^+$, 2.31; $H_3L^-/H_2L^{2-} + H^+$, 3.47; $H_2L^{2-}/HL^{3-} + H^+$, 4.54; and $HL^{3-}/L^{4-} + H^+$, 6.14. Ref. 6.

The analysis of the potentiometric experimental data allowed the calculation of β_{pqr} constants for the complex species formed, defined by means of the equilibria (*1*).

$$pH^+ + qM^{2+} + rL^{4-} \rightleftharpoons [H_pM_qL_r]^{(p+2q-4r)+} \qquad (1)$$

The model that best fits the experimental results for each cation is that which corresponds to the complex species indicated in Table I. Although models were tested that included the presence of complex species with an excess of ligand, the results indicate that they are not present in significant amounts, except for Cd(II). From the β_{pqr} constants and taking into account the β_{pr} constants of 2,6-TDTA acid[5,6] the formation constants (log K) of the complex species formed can readily be calculated according to the equilibria (*2*)-(*14*) given in Table I as well as the constants corresponding to the dimerization equilibria (*15*) and (*16*). Table I also includes the values of pKi corresponding to the protonated complex species (equilibria (*18*)-(*20*)), together with those of the equilibria (*17*), (*21*) and (*22*). For comparison purposes, data for log K and pKi are contrasted with data for *m*-PDTA acid with Cu(II),[3] Ni(II)[2] and Co(II).[1]

For the monomer complex species of Cu(II) (CuH_2L, $[CuHL]^-$ and $[CuL]^{2-}$), the values found for log K are in good agreement with those previously found at the same ionic strength and temperature.[5]

In accord with the conductimetric study (Figure 1), the values of log K for the monomer species $[MHL]^-$ and $[ML]^{2-}$ indicate that Cu(II) forms complexes that are much stronger than the remaining cations. The Irving–Williams order of complexation Cu(II) $\gg$ Ni(II) > Co(II) < Zn(II) is fulfilled (Table I). However, with the exception of Cu(II), the complexes in this case are weak, with small differences in the order of stability. The data of Table I also indicate that the dimeric species $[M_2HL_2]^{3-}$ and $[M_2L_2]^{4-}$ are more stable than the monomeric species $[MHL]^-$ and $[ML]^{2-}$, respectively (equilibria (*15*) and (*16*)). For the dimer species $[M_2HL_2]^{3-}$ and $[M_2L_2]^{4-}$ (log K, equilibria (*9*) and (*10*)) the Irving–Williams order of stability Cu(II) $\gg$ Ni(II) $\approx$ Co(II) < Zn(II), is practically fulfilled. However, such is not the case for the dimerization constants (equilibria (*15*) and (*16*)), where the order is Cu(II) < Ni(II) < Co(II) > Zn(II). This result is similar to that obtained with *m*-PDTA acid.[1-3] In the monomeric complexes, 2,6-TDTA acid, analogously to *m*-PDTA acid, behaves as a terdentate, bonding through an iminodiacetate group to the metal cation. The remainder of the coordination is completed by molecules of solvent.[11,12] In the dimer species the metal cation is bonded to two iminodiacetate groups of different ligands (Figure 2), as has been verified by X-ray structural analysis for the complexes[3] $[Cu_2(m\text{-}PDTA)_2]^{4-}$, $[Co_2(m\text{-}PDTA)_2]^{4-}$ and $[Ni_2(2,6\text{-}PDTA)_2]^{4-}$. The Irving–Williams order is related to ligand field stabilization energies and, in particular, the strength of the M–N bond. However, the dimerization process (equilibria (*15*) and (*16*)) is easier for Co(II), Ni(II) and Zn(II) than for Co(II). This may be accounted for, the coordination octahedra being more regular for Co(II), Ni(II) and Zn(II) than for Cu(II),[3] by the Jahn–Teller effect for Cu(II). The values of pKi for the species $[MHL]^-$ (equilibrium (*19*)) are consistent with a betainic proton bonded to an iminodiacetic group.[6,13,14] If these values are compared with pKi corresponding to equilibrium (*20*), (Table I), an increase is observed in the acidity corresponding to the formation of the dimer $[M_2L_2]^{4-}$, but contrary to the case of *m*-PDTA acid,[1-3] no clear difference is observed from the pKi values corresponding to the shift of the betainic protons of the species to form the dimer species $[M_2L_2]^{4-}$ (equilibrium (*20*)). This must be attributed to the repulsive effects of the methyl radical in the 2,6-TDTA acid complexes. In comparison with *m*-PDTA acid,[1-3] both values of log K (Table I) for the monomer complex species and for those of the dimers, the stability order 2,6-TDTA $\ll$ *m*-PDTA is found, and which must be attributed once again in the 2,6-TDTA acid to the repulsive effects of the methyl radical on the metallic cation in the monomer species and on both cations in the dimer species (Figure 2).

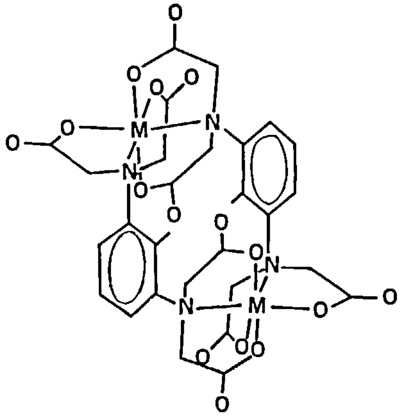

FIGURE 2 Structure proposed for the complex $[M_2L_2]^{4-}$.

The species distribution diagrams as a function of $-\log[H^+]$ show more clearly these differences in coordinating ability: for Co(II) (Figure 3a), Ni(II) (Figure 4a) and Zn(II) (Figure 5a) at $C_M = 2$ mM, the concentration of the monomer complex $[ML]^{2-}$ is lower than that of the dimer complex $[M_2L_2]^{4-}$, while, unlike Cu(II) (Figure 6a), the concentration of the monomer $[CuL]^{2-}$ is greater than that of the dimer $[Cu_2L_2]^{4-}$. This is due to the fact that the complex $[CuL]^{2-}$ is much stronger than the weak complexes $[CoL]^{2-}$, $[NiL]^{2-}$ and $[ZnL]^{2-}$. It can be observed that at $C_M = 2$ mM, pH 6, Co(II) is only complexed to 47.6%, Ni(II) 44.2% and Zn(II) 63.7%, while Cu(II) complexes 98.7%. The equilibria (*15*) and (*16*) (Table I) are displaced to the right and indicate that an increase in concentration facilitates the formation of the dimer species $[M_2HL_2]^{3-}$ and $[M_2L_2]^{4-}$ with respect to the monomer species $[MHL]^-$ and $[ML]^{2-}$; at pH 6, for Co(II) (Figure 3) the amount of dimer $[M_2L_2]^{2-}$ is 20.2 and 44.8% at $C_M = 2$ and 10 mM, respectively; for Ni(II) (Figure 4) 16.2 and 45.6%, respectively; for Zn(II) (Figure 5) 28.2 and 57.6%, respectively; for Cu(II) (Figure 6) 20.6 and 45.2%, respectively.

The diagrams also indicate that the species MH_2L and $[MHL]^-$ are transformed into $[MHL]^-$ and $[ML]^{2-}$ (equilibria (*18*) and (*19*)), respectively. Moreover, the species $[MHL]^-$ participates in a very significant manner in the dimerization process by way of equilibrium (*20*). Figures 3b, 4b, 5a and 6a show that equilibria (*21*) and (*22*) play an important role in the formation of the species $[ML]^{2-}$ and $[M_2L_2]^{4-}$, respectively, indicating also that the monoprotonated dimer species $[M_2HL_2]^{3-}$ is mainly formed by way of the equilibria

$$2M^{2+} + 2H_2L^{2-} \rightleftharpoons [M_2HL_2]^{3-} + 3H^+ \qquad (23)$$

$$2M^{2+} + 2HL^{3-} \rightleftharpoons [M_2HL_2]^{3-} + H^+ \qquad (24)$$

and that the non-protonated dimer species $[M_2L_2]^{4-}$ is also formed by way of the following equilibria.

$$2M^{2+} + 2HL^{3-} \rightleftharpoons [M_2L_2]^{4-} + 2H^+ \quad (25)$$

$$[M_2HL_2]^{3-} \rightleftharpoons [M_2L_2]^{4-} + H^+ \quad (26)$$

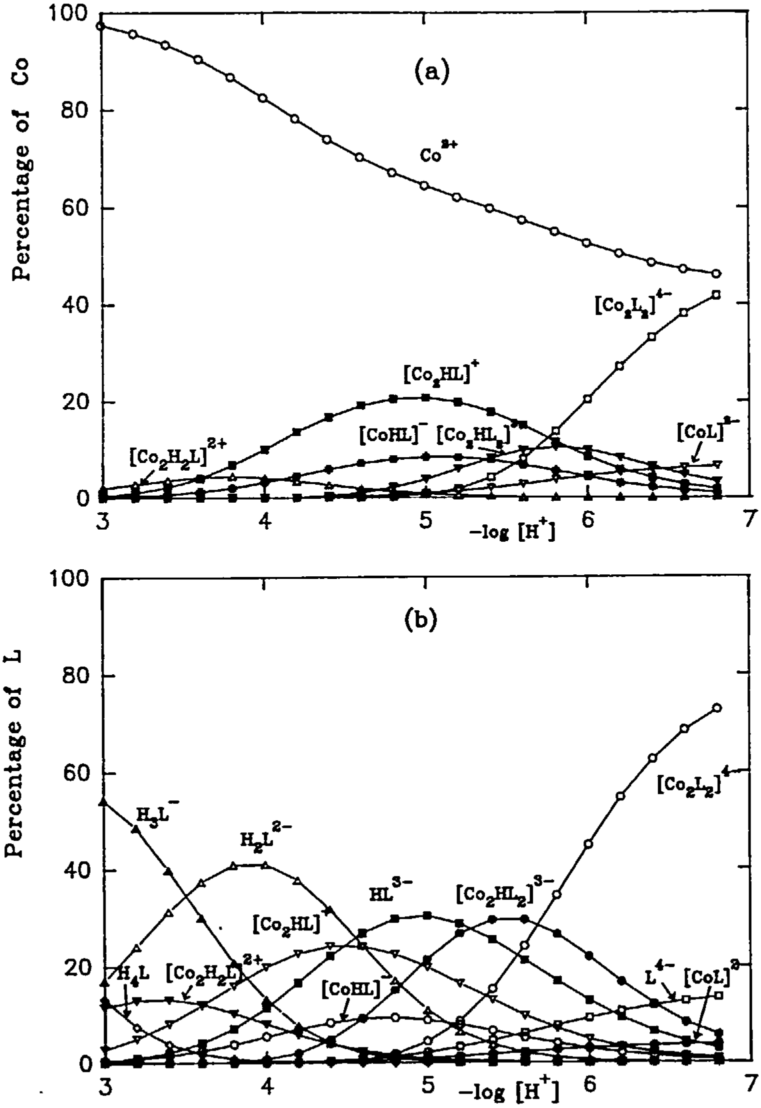

FIGURE 3 Species distribution as a function of $-\log[H^+]$ for the Co(II)-2,6-TDTA system (ligand: metal ratio 1:1): *a*, %Co, 2 mM; *b*, %L, 10 mM; calculated from the values of pKi and logK given in Table I.

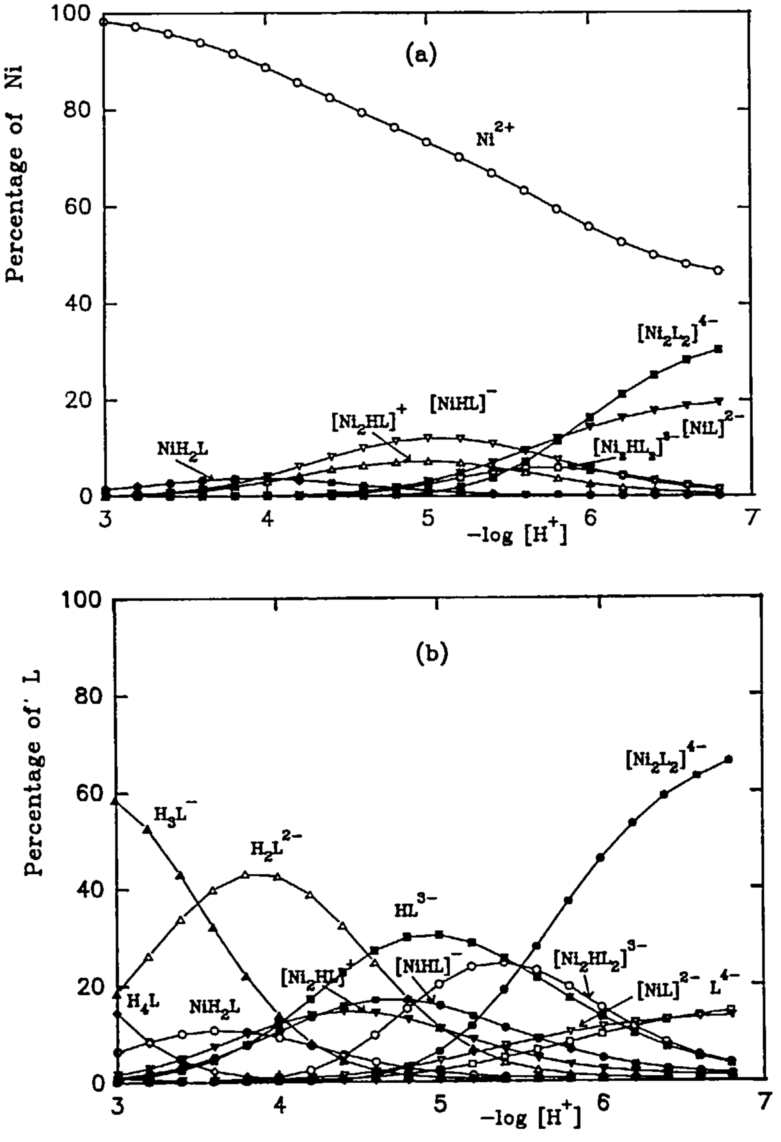

FIGURE 4 Species distribution as a function of $-\log[H^+]$ for the Ni(II)-2,6-TDTA system (ligand: metal ratio 1:1); *a*, %Ni, 2 mM; *b*, %L, 10 mM; calculated from the values of pKi and logK given in Table I.

The bimetallic species $[M_2H_2L]^{2+}$, $[M_2HL]^+$ and M_2L, where each iminodiacetic group of any one ligand is bonded to a different metallic atom,[11] are stable at low pH and are subsequently transformed into dimer species upon bonding to another species of the ligand by means of the equilibria below.

M = Co $[M_2H_2L]^{2+} \rightleftharpoons [M_2HL]^+ + H^+$ (*27*)

M = Co, Ni $[M_2HL]^+ + HL^{3-} \rightleftharpoons [M_2HL_2]^{3-} + H^+$ (*28*)

M = Zn $[M_2H_2L]^{2+} + HL^{3-} \rightleftharpoons [M_2HL_2]^{3-} + 2H^+$ (*29*)

M = Cu $[M_2H_2L]^{2+} \rightleftharpoons M_2L + 2H^+$ (*30*)

M = Cu $M_2L + HL^{3-} \rightleftharpoons [M_2L_2]^{4-} + H^+$ (*31*)

M = Cu $M_2L + L^{4-} \rightleftharpoons [M_2L_2]^{4-}$ (*32*)

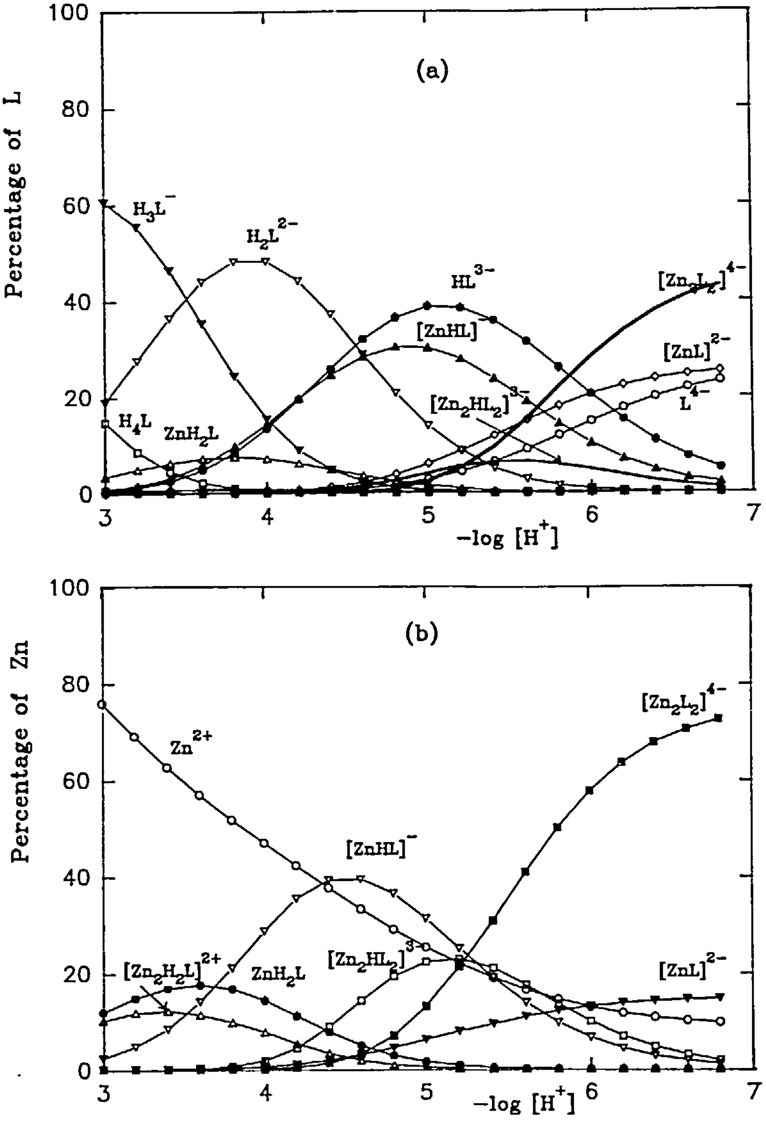

FIGURE 5 Species distribution as a function of $-\log[H^+]$ for the Zn(II)-2,6-TDTA system (ligand: metal ratio 1:1): *a*, %L, 2 mM; *b*, %Zn, 10 mM; calculated from the values of pKi and logK given in Table I.

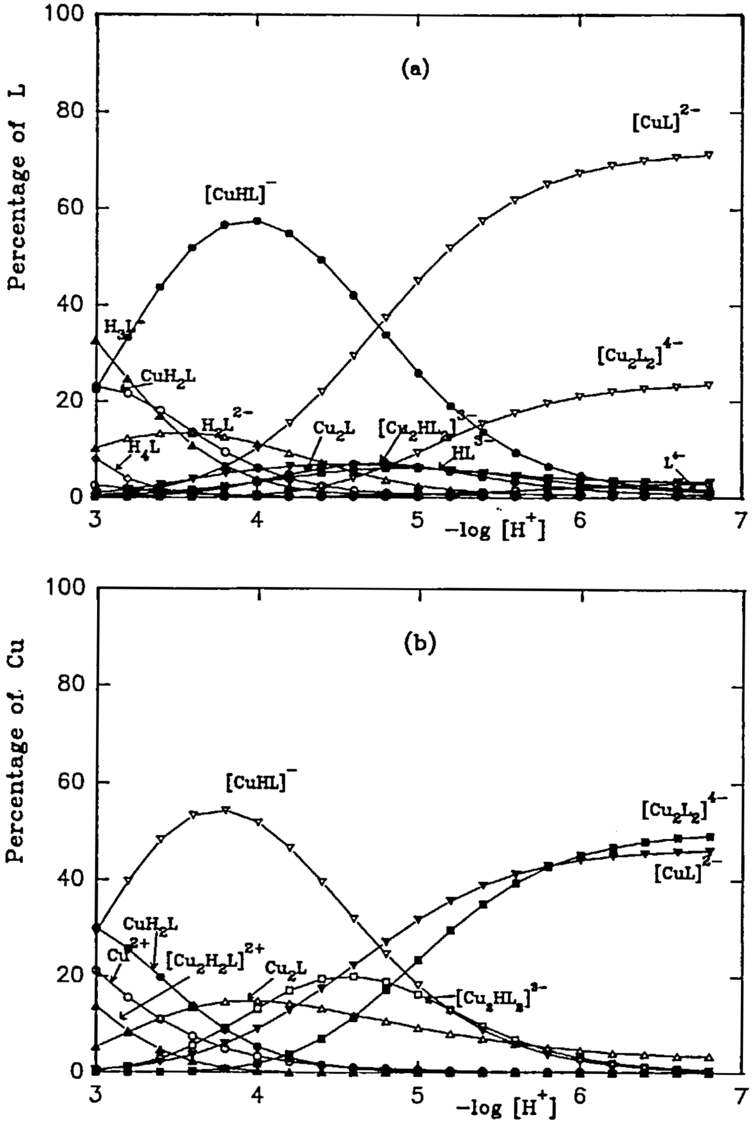

FIGURE 6 Species distribution as a function of $-\log[H^+]$ for the Cu(II)–2,6-TDTA system (ligand: metal ratio 1:1): *a*, %L, 2 mM; *b*, %Cu, 10 mM; calculated from the values of pKi and logK given in Table I.

Figures 3–6 also indicate that a concentrated solution with a ligand:metal ratio of 1:1 at pH 6 is suitable for the synthesis of crystalline salts of the dimer complexes $[M_2L_2]^{4-}$, analogously to *m*-PDTA[3] and 2,4-TDTA acids.[4]

Cd(II) and Mn(II) do not form dimeric species at the concentrations studied.

ACKNOWLEDGEMENTS

We wish to thank the Education Council of the Canary Islands Government (Grant 33/01.06.88) and the Spanish Ministry of Education and Science, Spain (DGICYT, Grant PB89-0401), for financial support. Felipe Brito thanks the DGICYT (Spanish Ministry of Education and Science) for financial support during his temporary Sabbatical stay at the Department of Inorganic Chemistry, University of La Laguna (Tenerife, Canary Islands).

REFERENCES

1. F. Brito, A. Mederos, P. Gili, S. Domínguez and P. Martín-Zarza, *J. Coord. Chem.*, **17**, 311 (1988).
2. F. Brito, A. Mederos, P. Gili, R. Guerra, S. Domínguez and M. Hernández-Padilla, *J. Coord. Chem.*, **20**, 169 (1989).
3. A. Mederos, P. Gili, S. Domínguez, A. Benítez, M.S. Palacios, M. Hernández-Padilla, P. Martín-Zarza, M.L. Rodríguez, C. Ruiz-Pérez, F.J. Lahoz, L.A. Oro, F. Brito, J.M. Arrieta, M. Vlassi and G. Germain, *J. Chem. Soc., Dalton Trans.*, 1477 (1990).
4. S. Domínguez, A. Mederos, P. Gili, A. Rancel, E. Rivero, F. Brito, M.L. Rodríguez, I. Brito and F. Lloret, to be published.
5. A. Mederos, A. Benítez, A. Rancel, R. Guerra, F. Brito, K. Bazdikian and J. Bruzal, *J. Coord. Chem.*, **15**, 85 (1986).
6. A. Mederos, A. Rancel, S. Domínguez, V. Herrera and A. Benítez, *An. Quim.*, in press.
7. G. Biedermann and L.G. Sillén, *Arkiv Kemi*, **5**, 425 (1953).
8. R.M. Smith and A.E. Martell, "Critical Stability Constants", Vol. 4, (Plenum Press, New York, 1976), p. 1.
9. F. Brito and N. Ingri, *An. Quim.*, **56B**, 165 (1960).
10. P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1195 (1985).
11. C. Ruiz-Pérez, M.L. Rodríguez, F.V. Rodríguez-Romero, A. Mederos, P. Gili and P. Martín-Zarza, *Acta Cryst.*, **C46**, 1405 (1990).
12. A. Mederos, J. Fuentes, E. Medina, P. Martín-Barroso and B. Rodríguez Ríos, *An. Quim.*, **76B**, 352 (1980).
13. A. Mederos, A. Rodríguez González and B. Rodríguez Ríos, *An. Quim.*, **69**, 601 (1973).
14. A. Mederos, F.G. Manrique, J.V. Herrera, M. Alvarez-Romero and J.M. Felipe, *An. Quim.*, **82B**, 133 (1986).