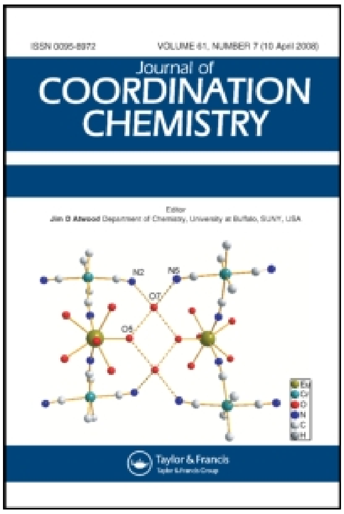

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COMPLEX SPECIES IN AQUEOUS SOLUTIONS OF *META*-PHENYLENEDIAMINE-*N,N,N′,N′*-TETRAACETIC ACID IN THE PRESENCE OF NICKEL(II)

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The complex species formed in aqueous solution between Ni(II) and *meta*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid were studied at 25°C and ionic strength 0.1 M in KCl. Potentiometric investigations were carried out at ligand:metal ratios 2:1, 1:1 and 1:2. The concentration of Ni(II) was 1 mM, 2 mM and 3 mM. The application of the least-squares computer program LETAGROP to the experimental potentiometric data indicates that the following complex species are formed (ligand, H_4C): NiH_2C (log K = 1.72); $NiHC^-$ (log K = 3.98); NiC^{2-} (log K = 5.26); $Ni_2C_2^{4-}$ (log K = 14.38); and Ni_2C (log K = 7.86). Compared with Cu(II), species with excess ligand are not present in any significant amounts. The dimer $Ni_2C_2^{4-}$ has been identified for the first time in potentiometric studies in aqueous solution.

Keywords: Nickel, phenylenediamine, multidentates, dimerization, stability constants

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. In the case of diaminetetramethylcarboxylic acid derivatives of *meta* or *para*-phenylenediamines only one nitrogen atom can coordinate to any metallic cation. These ligands can therefore coordinate two spheres, as has been proven by X-ray crystallographic determination of the structure[1] of the complex Cu_2(*p*-PDTA) (*p*-PDTA = *para*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid) and studies in aqueous solution of *p*-PDTA, *m*-PDTA (*meta*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid), 2,5-TDTA (2,5-toluenediamine-*N,N,N′,N′*-tetraacetic acid), 2,4-TDTA (2,4-toluenediamine-*N,N,N′,N′*-tetraaceticacid), 2,6-TDTA (2,6-toluenediamine-*N,N,N′,N′*-tetraacetic acid) and 2,6-PDTA (2,6-pyridinediamine-*N,N,N′,N′*-tetraacetic acid).[2-4] Complexes of the tipe M_2C (ligands, H_4C) are present. The formation of species with excess ligand is also possible, since each iminodiacetic group of the ligand is

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insufficient to coordinatively saturate the central ion, as confirmed by our studies in aqueous solution of the coordinating capacity of *m*-PDTA, *p*-PDTA and 2,5-TDTA acids with Cu(II)[2,3] and *m*-PDTA acid with Be(II).[5]

In the case of ligands derived from *m*-phenylenediamines, the special conformation of the ligand facilitates the formation of dimers, since the ligands may act as a bridge. This has been proven in the case of Schiff bases by means of X-ray diffraction analysis of the structure[6] of the complex Cu_2(sal-*m*-phen)$_2$ (sal-*m*-phen = *N,N'-m*-phenylenebis(salicylaldimine)), and by mass spectrometry for the complexes Co_2-(acac-*m*-phen)$_2$ and Cu_2(acac-*m*-phen)$_2$[7] (acac-*m*-phen = *N,N'-m*-phenylenebis(acetylacetoneimine)). In the case of diaminepolycarboxylic acids, evidence was found for the formation in the solid state of complexes with the 2:2 ligand:metal ratio[8] for *m*-PDTA acid with Ni(II), Co(II) and Cu(II), as was subsequently confirmed by X-ray diffraction structure analyses[9-11] of the complexes Cu_2(*m*-PDTA)$_2$, Co_2(*m*-PDTA)$_2$ and Ni_2(2,6-PDTA)$_2$. A spectrophotometric study[12] in aqueous solution of the system Cu(II)–*m*-PDTA indicated the formation of complex species in the ratio 2:2, but the potentiometric study in aqueous solution of the systems Cu(II)-*m*-PDTA[2], Cu(II)–2,4-TDTA[4], Cu(II)–2,6-TDTA[4] and Cu(II)–2,6-PDTA[4] (varying the concentration of metallic cation from 0.5 mM to 1.5 mM, and analysing the experimental data by means of the NERNST/LETA/GRAFICA version[13] of the LETAGROP program[14]), did not indicate the presence of significant amounts of such complexes. However, a similar study,[15] of the system Co(II)-*m*-PDTA, (varying the concentration of metallic cation from 1 mM to 2 mM) revealed for the first time in potentiometric studies the presence in aqueous solution of complex species with the ratio 2:2 for *m*-PDTA acid and its analogues. More recently, a similar study[9] of the system Cu(II)–*m*-PDTA, varying the concentration of metallic cation from 2 mM to 10 mM, revealed the presence of complex species $Cu_2C_2^{4-}$ in aqueous solutions, at concentrations $C_M > 2$ mM, in significant amounts. In the present work we studied the possible presence of the dimer complex species in aqueous solution for the system Ni(II)–*m*-PDTA. Previous studies of this system[16,17] did not take into account the possible presence of these species.

EXPERIMENTAL

The *m*-PDTA acid was prepared according to the method of Blasius and Olbrich.[18] 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.

The potentiometric titrations were carried out in aqueous solution at ionic strength 0.1 M in KCl and at 25 ± 0.05°C. A Radiometer 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 Biederman and Sillén,[19] the liquid junction potentials being found to be negligible within the margins of $[H^+]$ studied. It was found that pKw = 13.74, in excellent agreement with reported data.[20] A carbonate-free sodium hydroxide solution was prepared according to the method of Sillén[21] and standardized against potassium hydrogen phthalate. The Ni(II) solution (in the form of the chloride) was evaluated gravimetrically with dimethylglyoximate[22] and complexometrically.[23] KCl was prepared by recrystallization of KCl. KCl, $NiCl_2$ and NaOH, Merck, were of analytical grade.

Measurements were taken of the ligand in the presence of Ni(II) at ligand : metal ratios 2:1, 1:1 and 1:2. The concentration of Ni(II) was 1 mM, 2 mM and 3 mM.

Data Treatment

The experimental potentiometric data were analysed by means of the NERNST/LETA/GRAFICA version[13] of the LETAGROP program,[14] based on a generalized form of the least-squares method that establishes the best model and best values of the β_{pqr} constants by minimizing the function $U = \Sigma(Z_{exp} - Z_{calc})^2$, Z being the average number of dissociated protons for the concentration of ligand (Zc) or for the total concentration of metal (Z_B). The LETAGROP calculations also give standard deviations $\sigma(\log \beta_{pqr})$.[24] The computations were performed on a Burroughs 6700 computer (Facultad de Ciencias, Universidad Central de Venezuela). It was found that, under the experimental conditions used, hydrolysis of Ni(II) is negligible. The ionization constants of *m*-PDTA acid were previously obtained under the same experimental conditions.[2]

RESULTS AND DISCUSSION

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

$$pH^+ + qNi^{2+} + rH_4C \rightleftharpoons H_pNi_q(H_4C)_r^{(p+2q)+} \qquad (1)$$

The model that best fits the experimental results is that which corresponds to the complex species indicated in Table I. The validity of the same is proven in Figure 1,

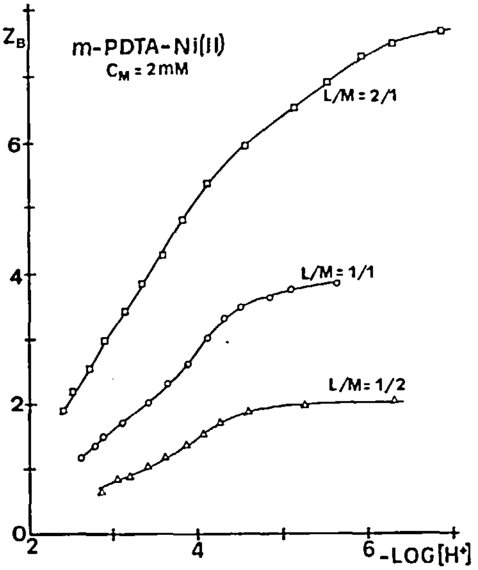


FIGURE 1 $Z_B(-\log[H^+])$ curves for the Ni(II)-*m*-PDTA system. Full curves are calculated using the constants β_{pqr} in Table I.

where excellent fit is observed between the experimental curves $Z_B(-\log[H^+])$ and those calculated from the β_{pqr} values given 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. From the β_{pqr} constants and taking into account the β_{pr} constants of *m*-PDTA acid,[2] the stability constants of the complex species formed can readily be calculated according to the equilibria given in Table I. For comparison purposes, they are contrasted with data for Cu(II)[2,9] and Co(II).[15]

TABLE I
Stability Constants for *m*-PDTA acid with Ni(II) at 25°C and $I = 0.1$ M in KCl.

			log K		
pqr	$-\log\beta_{pqr}$	Equilibrium	Ni(II)[a]	Co(II)[b]	Cu(II)[c]
−211	3.18 ± 0.13	(*2*) $H_2C^{2-} + M^{2+}/MH_2C$	1.72	2.06	4.47
−311	5.91 ± 0.02	(*3*) $HC^{3-} + M^{2+}/MHC^-$	3.98	3.33	6.65
−411	10.38 ± 0.07	(*4*) $C^{4-} + M^{2+}/MC^{2-}$	5.26	5.02	8.28
−822	16.90 ± 0.03	(*5*) $2C^{4-} + 2M^{2+}/M_2C_2{}^{4-}$	14.38	12.93	17.92
−421	7.80 ± 0.20	(*6*) $C^{4-} + 2M^{2+}/M_2C$	7.86		12.07
		(*7*) $2MC^{2-}/M_2C_2{}^{4-}$	3.86	2.89	1.36
		(*8*) $M^{2+} + MC^{2-}/M_2C$	2.58		3.85

	pKi		
Equilibrium	Ni(II)[a]	Co(II)[b]	Cu(II)[c]
(*9*) $H_2C^{2-} + M^{2+}/MHC^- + H^+$	1.02	1.67	−1.65
(*10*) $MH_2C/MHC^- + H^+$	2.73	3.73	2.82
(*11*) $MHC^-/MC^{2-} + H^+$	4.47	4.06	4.18
(*12*) $2MHC^-/M_2C_2{}^{4-} + 2H^+$	5.08	5.23	7.00
(*13*) $H_2C^{2-} + M^{2+}/MC^{2-} + 2H^+$	5.49	5.73	2.47
(*14*) $2H_2C^{2-} + 2M^{2+}/M_2C_2{}^{4-} + 4H^+$	7.12	8.57	3.58
Number of Titrations	9		
Number of experimental points	193		
Standard deviation $\sigma(Z)$	0.020		
$-\log[H^+]$ range	2.29–9.31		

[a] This work. [b] From Ref. 2. [c] From Ref. 9.

The values of pK_i corresponding to the ionization of the protonated complex species (equilibria (*10*)–(*12*)) are presented in Table I, as well as data for the equilibria (*9*), (*13*) and (*14*). These values are readily obtained from the values of log β_{pqr} or log K (Table I) and from the pK_i data for *m*-PDTA acid.[2]

The values found for log K (species NiH_2C, $NiHC^-$ and Ni_2C, Table I) are in good agreement with those previously found at the same ionic strength and temperature,[16,17] but log K for the complex NiC^{2-} (Table I) is more affected by the presence of the dimer complex $Ni_2C_2{}^{4-}$, which has been identified for the first time in potentiometric studies in aqueous solution. Compared with Cu(II),[2] species with excess ligand are not present in any significant amounts (to which fact must also be attributed the lower stability of the Ni(II) complexes). The bimetallic species Ni_2C is much less stable than the corresponding complex of Cu(II), Cu_2C (Table I). Its stability is more influenced by the great stability of the dimer species $Ni_2Cu_2{}^{4-}$, as can be observed in the diagram of species distribution (ligand:metal ratio 1:2, Figure

2) where, despite the excess metallic cation, the percentage of the dimeric species $Ni_2C_2^{4-}$ at pH 6 is almost five times greater than that of Ni_2C (34.8% *versus* 7.7%, respectively). It is also observed that with an excess of metallic cation (1 : 2), the monomeric species NiC^{2-} (11%) is found in a greater proportion than Ni_2C, in accordance with the low stability of the latter.

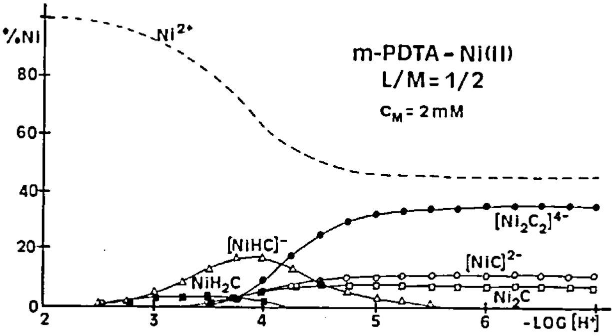
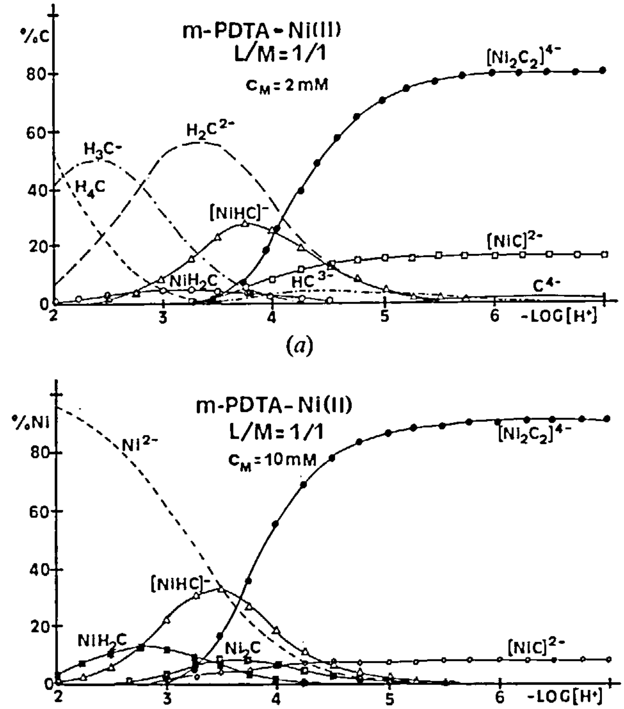


FIGURE 2 Species distribution (%Ni), as a function of $-\log[H^+]$ for the Ni(II)-*m*-PDTA system (ligand:metal ratio 1:2).

The diagram of distribution of species (Figure 3a, % C *vs* $-\log[H^+]$, $C_M = 2\,mM$; Figure 3b, % Ni *vs* $-\log\,[H^+]$, $C_M = 10\,mM$) indicates that the species NiH_2C is formed in a small proportion mainly according to equilibrium (*1*). The species NiH_2C is transformed into species $NiHC^-$ by the loss of a fundamentally carboxylic proton (equilibrium (*10*)). However, Figure 3a indicates that the species $NiHC^-$ mainly originates from the ligand species H_4C and H_3C^-. The value of pK_i for the monopronated species $NiHC^-$ (equilibrium (*11*)) is consistent with a betainic proton bonded to an iminodiacetic group,[2,25,26] the Ni(II) ion being bonded to the other iminodiacetic group (very strong acidity upon displacement by the Ni(II) of the betainic proton from the ligand species H_2C^{2-} (equilibrium (*9*)).

The data presented in Table I (equilibrium (*7*), log K = 3.86) indicate that the dimeric species $Ni_2C_2^{4-}$ is more stable than the monomer NiC^{2-}. This result is in agreement, as expected, with the values of pK_i also given in Table I. If a comparison is made of the values of pK_i corresponding to the formation of the dimeric species $Ni_2C_2^{4-}$ and the monomeric species NiC^{2-}, starting from the monoprotonated species $NiHC^-$, an increase in acidity is observed (equilibrium (*12*) *versus* equilibrium (*11*)) as $Ni_2C_2^{4-}$ is formed. This increase is confirmed by comparing the values of pK_i for equilibrium (*14*) *versus* equilibrium (*13*), corresponding to the direct formation of the monomeric and dimeric species from ligand H_2C^{2-}, the most important ligand species at pH 3 to 4 (Figure 3a). That is, the complexed Ni(II) ion in the monoprotonated species $NiHC^-$ displaces the betainic proton of another $NiHC^-$ species and *vice versa*, the dimeric $Ni_2C_2^{4-}$ being formed (equilibrium (*12*)). Each Ni(II) ion is therefore bonded in $Ni_2C_2^{4-}$ to two iminodiacetic groups of different ligands, as shown in the structure proposed in Figure 4. This explains the increase in the stability of the dimer $Ni_2C_2^{4-}$ with respect to the monomer NiC^{2-}, in which the Ni(II) ion is bonded to a single iminodiacetic group. The special conformation of the ligands derived from *m*-phenylenediamines facilitates the formation of such species (Figure 4), as has been proven in the solid state by X-ray diffraction structure analysis[9,11] of the complexes $Cu_2(m\text{-PDTA})_2$, $Co_2(m\text{-PDTA})_2$ and $Ni_2(2,6\text{-PDTA})_2$.



(a)

(b)

FIGURE 3 Species distribution as a function of $-\log[H^+]$ for the Ni(II)-*m*-PDTA system (ligand:metal ratio 1:1): *a*: % C, 2 mM; *b* % Ni, 10 mM.

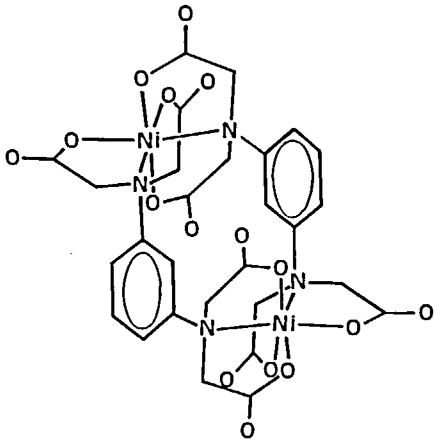


FIGURE 4 Structure proposed for the complex $Ni_2C_2^{4-}$.

Figures 3a ($C_M = 2$ mM) and 3b ($C_M = 10$ mM) indicate that an increase in concentration facilitates the formation of $Ni_2C_2^{4-}$ with respect to NiC^{2-}, as expected (equilibrium (7)); at pH 6, $C_M = 2$ mM, the percentage of $Ni_2C_2^{4-}$ is 80% and that of NiC^{2-} 16.6%; at $C_M = 10$ mM, the percentages are 91% and 8%, respectively. The diagrams indicate that $Ni_2C_2^{4-}$ is much more stable than NiC^{2-}. The diagrams also indicate that $NiHC^-$ is readily transformed into NiC^{2-} (equilibrium (*11*)) or $Ni_2C_2^{4-}$ (equilibrium (*12*)), although Figure 3a reveals that the complexes NiC^{2-} and $Ni_2C_2^{4-}$ are mainly formed in accordance with equilibria (*13*) and (*14*).

In Table I it is observed that the order of complexation of Irving and Williams is fulfilled for the complexes MHC^- and MC^{2-} (Cu(II) $\gg$ Ni(II) > Co(II), equilibria (*3*) and (*4*)) as well as for the dimeric complexes $M_2C_2^{2-}$ (Cu(II) > Ni(II) > Co(II), equilibrium (*5*)). Such is however not the case for the dimerization constants (equilibrium (*7*)), where the order is Ni(II) > Co(II) > Cu(II). In the monomeric complexes, *m*-PDTA acid behaves as a terdentate ligand, bonding an iminodiacetic group to the metallic cation. The remainder of the coordination sphere of the metallic cation is completed with molecules of solvent, in a way similar to the complex Cu_2C of *p*-PDTA acid, as revealed by X-ray diffraction analysis of the structure.[1] The Irving–Williams order is related to the stabilization energies of the ligand field, and in particular to the strength of the M–N bond. However, the dimerization process (equilibrium (*7*)) is easier for Ni(II) and Co(II) than for Cu(II). As can be readily observed in the crystalline structures of the dimeric species Co_2(*m*-PDTA)$_2$[10] and Ni_2(2,6-PDTA)$_2$,[11] the coordination octahedra of Co(II) and Ni(II) are more regular than those corresponding to Cu(II) in the dimeric complex Cu_2(*m*-PDTA)$_2$.[9] In other words, the dimerization is influenced by the Jahn–Teller effect. This influence effect must be taken into account whether the dimerization is achieved *via* the non-protonated complexes MC^{2-} (equilibrium (*7*)), or the monoprotonated complexes MHC^- (equilibrium (*12*)). The values of pKi for the species MHC^- (equilibrium (*11*)) are consistent (*vide supra*) with a betainic proton bonded to an iminodiacetic group.[25,26] If these values are compared with pKi corresponding to equilibrium (*12*) (Table I), an increase is observed in the acidity corresponding to the formation of the dimer $M_2C_2^{4-}$, but this increase in the acidity follows the order Cu(II) $\ll$ Co(II) < Ni(II). The betainic proton of MHC^- is displaced with more difficulty in the case of Cu(II) to form $M_2C_2^{4-}$, due to the Jahn–Teller effect of the d^9 cations, and the acidity is weaker.

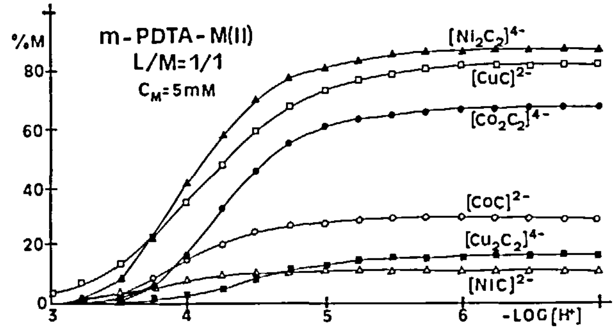


FIGURE 5 Percentages of formation (% M *versus* [$-\log$ [H^+]) of monomeric species MC^{2-} and dimeric species $M_2C_2^{4-}$ for Ni(II), Co(II) and Cu(II) (ligand:metal ratio 1:1, 5 mM).

The order Ni(II) > Co(II) > Cu(II) corresponding to the formation of the dimeric species $M_2C_2^{4-}$ starting from MC^{2-} is illustrated in Figure 5, where the percentages of formation of monomeric and dimeric species of Ni(II), Co(II) and Cu(II) at the ligand:metal ratio 1:1 at $C_M = 5\,\text{mM}$ and pH 6 are compared: $Ni_2C_2^{4-}$ (87%) $> Co_2C_2^{4-}$ (67%) $\geqslant Cu_2C_2^{4-}$ (16%) for dimeric species, whereas for the monomeric species the order is NiC^{2-} (11%) $< CoC^{2-}$ (30%) $\leqslant CuC^{2-}$ (83%).

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