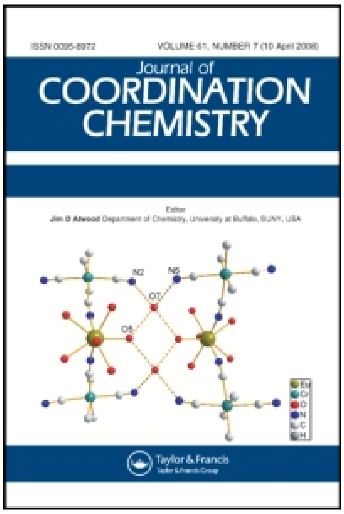

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COMPLEX SPECIES IN AQUEOUS SOLUTIONS OF *META*-PHENYLENEDIAMINE-*N,N,N′,N′*-TETRAACETIC ACID IN THE PRESENCE OF COBALT(II)

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The complex species formed in aqueous solution between Co(II) and *meta*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid were studied at 25° and ionic strength 0.1 M in KCl. Potentiometric investigations were carried out at metal : ligand ratios 2 : 1, 1 : 1 and 1 : 2. The concentration of Co(II) was 1 mM or 2 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) : CoH_2C (log K = 2.06); $CoHC^-$ (log K = 3.33); CoC^{2-} (log K = 5.02); and $Co_2C_2{}^{4-}$ (log K = 12.93). Compared with Cu(II), species with excess of ligand and excess of metal are not present in significant amounts. The dimer $Co_2C_2{}^{4-}$ has been identified for the first time in solution.

Keywords: Phenylenediamine, multidentates, cobalt, dimers, stability constants

INTRODUCTION

The preparation of coodinating agents derived from aromatic diamines is of special interest, since the use of nitrogen atoms for coodination to a single cation is directly related to their situation in *ortho*, *meta* or *para* positions. Thus, in the case of diaminepolycarboxylic acids, with derivatives of *ortho*-phenylenediamines, the greater proximity of the nitrogen atoms permits the simultaneous coordination of both to the same metallic cation. This has been established by the X-ray crystallographic determination of the structure of the complex Co(II)–(*o*-PDTA)[1] (*o*-PDTA = *o*-phenylenediamine-*N,N,N′,N′*,-tetraacetic acid), confirming the studies in aqueous solution of the coordinating capacity of the *o*-PDTA acid, 3,4-TDTA acid (3,4-TDTA = 3,4-toluenediamine-*N,N,N′,N′*,-tetraacetic) and 4-Cl-*o*-PDTA acid (4-Cl-*o*-PDTA = 4-chloro-1,2-phenylenediamine-*N,N,N′,N′*,-tetraacetic).[2–6] On the other hand the diaminepolycarboxylic acid derivatives of *meta* or *para*-phenylenediamines can only coordinate one nitrogen atom to any one metallic cation. These ligands can therefore coordinate two spheres, as has been proven in the preparation of bimetallic species in the solid state and studies in aqueous solution for *m*-PDTA

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(*m*-PDTA = *m*-phenylenediamine-*N*,*N*,*N*′,*N*′,-tetraacetic) and *p*-PDTA acids (*p*-PDTA = *p*-phenylenediamine-*N*,*N*,*N*′,*N*′,-tetraacetic).[7,8] Complexes of the M_2C type (ligands, H_4C), as well as the formation of species with excess ligand are also possible, since each iminodiacetic group of the ligand is insufficient to coordinatively saturate the central ion, as confirmed by our studies in aqueous solution of the coordinating capacity of *m*-PDTA and *p*-PDTA acids with Cu(II)[8] and Be(II).[9]

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[10] of the complex Cu_2(sal-*m*-phen)$_2$ (sal-*m*-phen = *N*,*N*′,-metaphenylenebis(salicylaldimine)), and by mass spectrometry for the complexes Co_2(acac-*m*-phen)$_2$ and Cu_2(acac-*m*-phen)$_2$[11] (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[12] for *m*-PDTA acid with Ni(II), Co(II) and Cu(II), as was subsequently confirmed by X-ray diffraction structure analyses[13,14] of the complexes Cu_2(*m*-PDTA)$_2$ and Ni_2(2,6-PDTA)$_2$ (2,6-PDTA = 2,6-pyridinediamine-*N*,*N*,*N*′,*N*′,-tetraacetic acid). A spectrophotometric study 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,[8] Cu(II)-2,4-TDTA[16] (2,4-TDTA = 2,4-toluenediamine-*N*,*N*,*N*′,*N*′,-tetraacetic acid), Cu(II)-2,6-TDTA[16] (2,6-TDTA = 2,6-toluenediamine-*N*,*N*,*N*′,*N*′,-tetraacetic acid) and Cu(II)-2,6-PDTA[16] (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[17] of the LETRAGROP program[18]), did not indicate the presence of significant amounts of such complexes. However, a similar study, reported below, 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. Previous studies of the system Co(II)-*m*-PDTA[19,20] did not take into account the possible presence of these species.

EXPERIMENTAL

The *m*-PDTA acid was prepared according to the Blasius and Olbrich method.[21] 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°. 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 Bierderman and Sillén,[22] 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.[23] A carbonate-free sodium hydroxide solution was prepared according to the method of Sillén[24] and standardized against potassium hydrogen phthalate. The Co(II) solution (in the form of the chloride) was evaluated electrolytically.[25] KCl, $CoCl_2$ and NaOH, Merck, were of analytical grade.

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

Data treatment

The experimental potentiometric data were analysed by means of the NERNST/LETA/GRAFICA version[17] of the LETAGROP program,[18] 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 $U = \sum (Z_{exp} - Z_{calc})^2$, Z being the average number of dissociated protons for the concentration of ligand (Z_C) or for the total concentration of metal (Z_B). The LETAGROP calculations also give standard deviations $\sigma(Z)$ and $\sigma(\log \beta_{pqr})$.[26] 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 Co(II) is negligible. The ionization constants of *m*-PDTA acid were previously obtained under the same experimental conditions.[8]

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*)

$$p\,H^+ + q\,Co^{2+} + r\,H_4C \rightleftharpoons H_pCo_q(H_4C)_r^{(p+2q)+} \qquad (1)$$

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, where excellent fit is observed between the experimental curves $Z_c(-\log [H^+])$ 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 and an excess of metal, 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,[8] 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).[8]

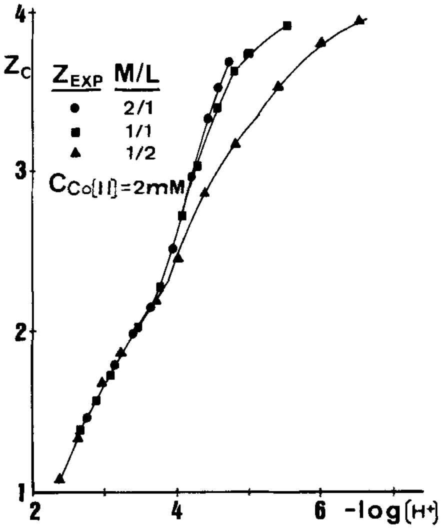

FIGURE 1 $Z_C(-\log[H^+])$ curves of the Co(II)-*m*-PDTA system. Full curves are calculated using the constants β_{pqr} in Table I.

The values of $pK_i[= -\log K_i]$ corresponding to the ionization of the protonated complex species (equilibria (*3*)–(*5*)) are presented in Table I, as well as data for the equilibria (*2*), (*6*) and (*7*).

$$H_2C^{2-} + Co^{2+} \rightleftharpoons CoHC^{-} + H^{+} \tag{2}$$

$$H_2C^{2-} + Co^{2+} \rightleftharpoons CoC^{2-} + 2\,H^{+} \tag{6}$$

$$2H_2C^{2-} + 2\,Co^{2+} \rightleftharpoons Co_2C_2^{4-} + 4\,H^{+} \tag{7}$$

These values are readily obtained from the values of $\log \beta_{pqr}$ or log K (Table I) and from the pK_i data for acid *m*-PDTA.[8]

TABLE I

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

pqr	$-\log \beta_{pqr}$	Equilibrium	log K	log K (Cu(II))
−211	2.84 ± 0.10	$H_2C^{2-} + Co^{2+}/CoH_2C$	2.06	4.47
−311	6.56 ± 0.08	$HC^{3-} + Co^{2+}/CoHC^{-}$	3.33	6.65
−411	10.62 ± 0.04	$C^{4-} + Co^{2+}/CoC^{2-}$	5.02	8.22
−822	18.35 ± 0.08	$2C^{4-} + 2Co^{2+}/Co_2C_2^{4-}$	12.93	
		$2CoC^{2-}/Co_2C_2^{4-}$	2.89	

Equilibrium	pK_i
(2) $H_2C^{2-} + Co^{2+}/CoHC^{-} + H^{+}$	1.67
(3) $CoH_2C/CoHC^{-} + H^{+}$	3.73
(4) $CoHC^{-}/CoC^{2-} + H^{+}$	4.06
(5) $2CoHC^{-}/Co_2C_2^{4-} + 2H^{+}$	5.23
(6) $H_2C^{2-} + Co^{2+}/CoC^{2-} + 2H^{+}$	5.73
(7) $2H_2C^{2-} + 2Co^{2+}/Co_2C_2^{4-} + 4H^{+}$	8.57

Number of titrations	6
Number of experimental points	114
Standard deviation σ(Z)	0.023
$-\log[H^{+}]$ range	2.40–6.53

In Table I it is observed that complexes with Cu(II) are more stable than those of Co(II), as expected. Likewise, by comparison with Cu(II),[8] complex species with excess of ligand and with excess of metal are not present in any significant amounts (to which fact must also be attributed the lesser stability of the Co(II) complexes). The species Co_2C was previously identified,[19,20] during work when a great excess of metallic cation (10 : 1–15 : 1) was employed.

The most important result of this study is the confirmation in aqueous solution, for the first time, of the presence of the dimer $Co_2C_2^{4-}$ with diaminopolycarboxylic ligands derived from *m*-phenylenediamines. The special conformation of the ligand facilitates the formation of such species (Figure 2), as has been proven in solid state by means of X-ray diffraction determinations[13,14] of the structure for the complexes $Cu_2(m\text{-PDTA})_2$ and $Ni_2(2,6\text{-PDTA})_2$.

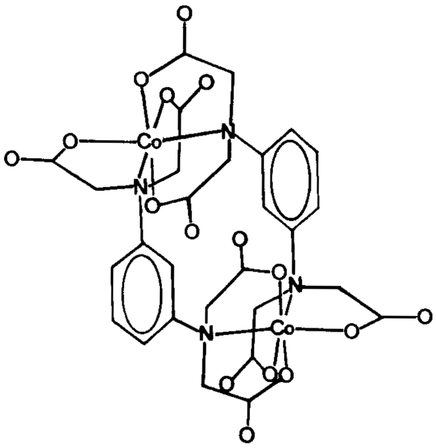

FIGURE 2 Structure proposed for the complex $Co_2C_2^{4-}$.

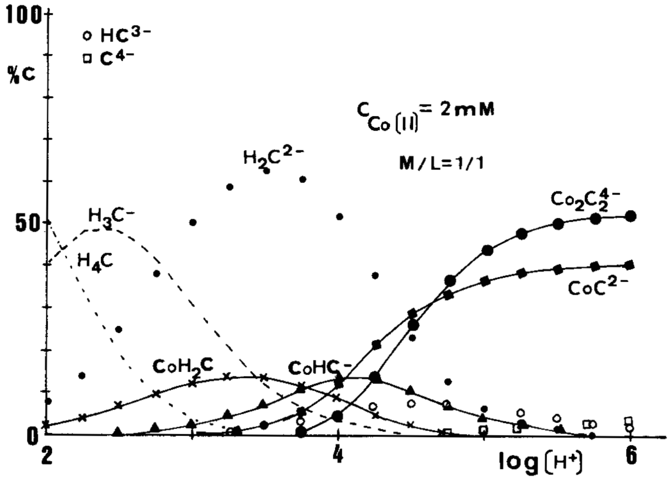

FIGURE 3 Species distribution (%C) as a function of $-\log [H^+]$ for the Co(II)-*m*-PDTA system.

The data presented in Table I (log K = 2.89) indicate that the dimeric species $Co_2C_2^{4-}$ is more stable than the monomeric species CoC^{2-}. This result is in agreement, as expected, with the values of pK_i also given in Table I; the value of pK_i for the monoprotonated species $CoHC^-$ is consistent with a betainic proton bonded to an iminodiacetic group,[27,28] the Co(II) being bonded to the other iminodiacetic group (very strong acidity upon displacement by the Co(II) of a betainic proton, equilibrium (*2*)). If a comparison is made of the values of pK_i corresponding to the formation of the dimeric species $Co_2C_2^{4-}$ and the monomeric species CoC^{2-}, starting from the monoprotonated species $CoHC^-$, an increase in acidity is observed (equilibrium (*5*) versus equilibrium (*4*)) as the species $Co_2C_2^{4-}$ is formed. This increase is confirmed by comparing the values of pK_i of equilibrium (*7*) versus equilibrium (*6*), 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 (a diagram of distribution of species is shown in Figure 3). That is, the complexed Co(II) in the monoprotonated species $CoHC^-$ displaces the betainic proton of another $CoHC^-$ species and *vice versa*, the dimeric species $Co_2C_2^{4-}$ being formed (equilibrium (*5*)). Each Co(II) is therefore bonded in $Co_2C_2^{4-}$ to two iminodiacetic groups of different ligands, as shown in Figure 2; this explains the increase in the stability of this species with respect to the monomer CoC^{2-}, in which the Co(II) is bonded to a single iminodiacetic group.

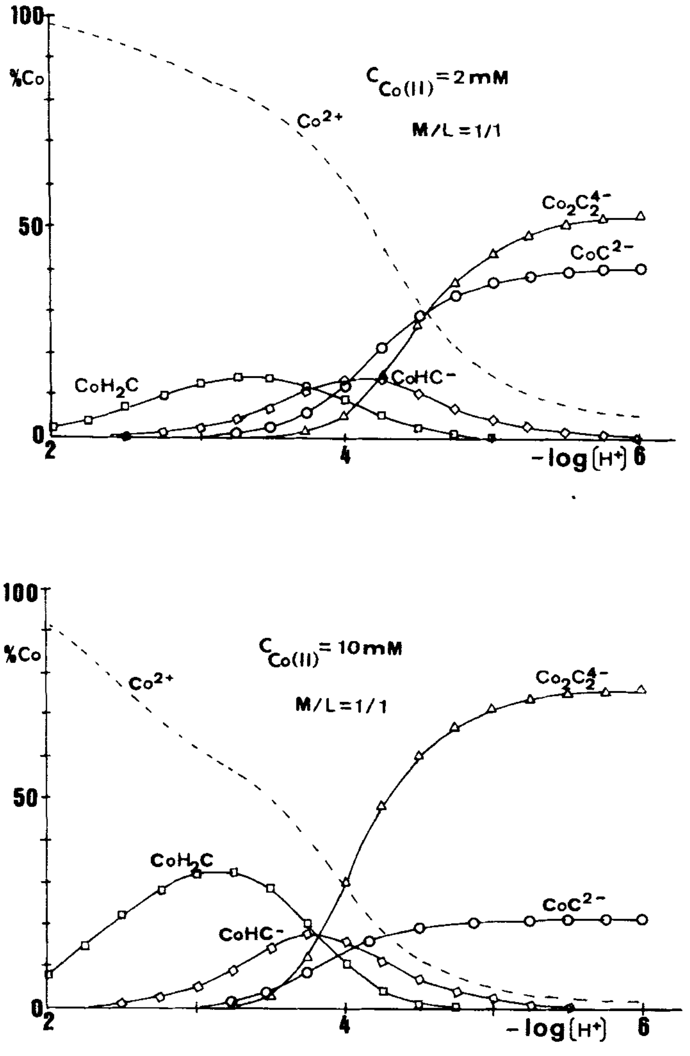

FIGURE 4 Species distribution (%Co) as a function of $-\log [H^+]$ for the Co(II)-*m*-PDTA system: *a*: 2 mM; *b*: 10 mM.

Figures 4*a* (concentration 2 mM) and 4*b* (concentration 10 mM) indicate that increase in concentration facilitates the formation of the dimeric species $Co_2C_2^{4-}$ with respect to the monomeric species CoC^{2-}, as expected. Therefore, the absence of the species $Cu_2C_2^{4-}$ in the case of the Cu(II) at a concentration of 1.5 mM,[8] does not rule out the possibility that $Cu_2C_2^{4-}$ may be found in aqueous solution at higher concentrations. These studies are, of course, limited by the solubility of the ligand.

Figures 3 and 4 also indicate that the species $CoHC^-$ mainly originates from the diprotonated species CoH_2C, formed according to equilibrium (*1*), by the loss of a fundamentally carboxylic proton (equilibrium (*3*)). The species $CoHC^-$ is readily transformed into CoC^{2-} or $Co_2C_2^{4-}$, although Figure 3 reveals that the complexes CoC^{2-} and $Co_2C_2^{4-}$ are mainly formed in accordance with equilibria (*6*) and (*7*). The species distributions also indicate that, mainly at low concentrations (2 mM), the monomeric species is formed before the dimeric one.

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