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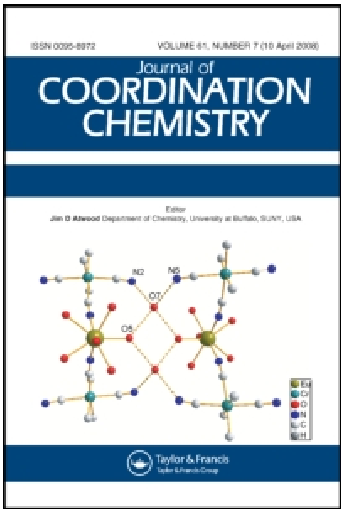

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A. Mederos[a]; S. Dominguez[a]; M. Hernandez-Padilla[a]; F. Brito[b]
[a] Departamento de Quimica Inorganica, Universidad de La Laguna, Tenerife, Canary Islands, Spain [b] Laboratorio de Equilibrios en Solution, Escuela de Quimica, Facultad de Ciencias,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

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NOTE

COMPLEX SPECIES IN AQUEOUS SOLUTIONS OF 4-CHLORO-1,2-PHENYLENEDIAMINE-*N,N,N',N'*,-TETRAACETIC ACID WITH MAGNESIUM(II), CALCIUM(II), STRONTIUM(II), BARIUM(II), ZINC(II) AND CADMIUM(II).

A. MEDEROS*, S. DOMINGUEZ, M. HERNANDEZ-PADILLA

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

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The coordination in aqueous solution of 4-chloro-1,2-phenylenediamine-*N,N,N',N'*-tetraacetic acid (4-Cl-*o*-PDTA) with Be(II) and with the transition metal cations cobalt(II), nickel(II) and copper(II) was reported in earlier publications.[1,2] In this note a study is presented of the coordination in aqueous solution (25°C, I = 0.1 M in KCl) of 4-Cl-*o*-PDTA acid with magnesium(II), calcium(II), strontium(II), barium(II), zinc(II) and cadmium(II).

Keywords: EDTA analogues, alkaline earths, zinc, cadmium, complexes, stability constants

EXPERIMENTAL

The monosodium salt of 4-Cl-*o*-PDTA acid was prepared according to a published method.[3] The metal solutions (in the form of chlorides) were evaluated complexometrically. The apparatus and titration procedures were those used in an earlier report.[2] Measurements were made with the ligand in the presence of metallic cation at the following concentrations and ligand : metal ratios: C_M = 1 mM (ratio 1 : 1), C_M = 2 mM (ratios 2 : 1, 1 : 1 and 1 : 2) and C_M = 3 mM (ratio 1 : 1). The experimental potentiometric data were analysed by means of the least-squares computer programs LETAGROP (on a UNISYS A10 computer, Universidad Central de Venezuela) MINIQUAD (on a DIGITAL VAX 11/780 computer, Universidad de La Laguna).

RESULTS AND DISCUSSION

The model that best fits the experimental results is that which corresponds to the complex species indicated in Table I ($[MHL]^-$ and $[ML]^{2-}$, ligand H_4L). From the

* Author for correspondence.

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TABLE I

Stability constants for the complexes of 4-Cl-*o*-PDTA with magnesium(II), calcium(II), strontium(II), barium(II), zinc(II) and cadmium(II) (25°C; I = 0.1 M in KCl).

MINIQUAD PROGRAM	Complex	Mg(II)	Ca(II)	Sr(II)	Ba(II)	Zn(II)	Cd(II)
$\log \beta_{011}$	$[ML]^{2-}$	6.16 ± 0.01	8.17 ± 0.01	5.53 ± 0.04	4.21 ± 0.01	12.35 ± 0.04	12.15 ± 0.01
$\log \beta_{111}$	$[MHL]^{-}$	9.25 ± 0.07	11.23 ± 0.02	9.04 ± 0.03	8.29 ± 0.06	15.54 ± 0.05	14.58 ± 0.01
log K	$[ML]^{2-}$	6.16	8.17	5.53	4.21	12.35	12.15
log K	$[MHL]^{-}$	3.30	5.27	3.08	2.33	9.59	8.62
pK_i	$[MHL]^{-}$	3.09	3.06	3.50	4.08	3.19	2.43
No. of titrations/No. of experimental points		5/81	5/111	5/108	5/92	5/79	5/90
R factor		0.0082	0.0065	0.0047	0.0067	0.0050	0.0025
Standard deviation (x 10^{-5})		2.3242	1.8387	1.3708	2.0068	1.6298	0.7962
$-\log[H^+]$ range		3.4–7.3	3.0–6.7	3.5–9.5	3.5–10.5	2.3–11.0	2.3–8.5
LETAGROP PROGRAM	complex	Mg(II)	Ca(II)	Sr(II)	Ba(II)	Zn(II)	Cd(II)
$\log \beta_{011}$	$[ML]^{2-}$	6.13 ± 0.02	8.18 ± 0.01	5.51 ± 0.02	4.15 ± 0.04	12.34 ± 0.02	12.16 ± 0.02
$\log \beta_{111}$	$[MHL]^{-}$	9.23 ± 0.17	11.28 ± 0.05	8.98 ± 0.12	8.07 (< 8.30)	15.48 ± 0.03	14.55 ± 0.02
log K	$[ML]^{2-}$	6.13	8.18	5.51	4.15	12.34	12.16
log K	$[MHL]^{-}$	3.33	5.38	3.08	2.30	9.58	8.65
pK_i	$[MHL]^{-}$	3.10	3.10	3.47	4.05	3.14	2.39
No. of titrations/No. of experimental points		5/82	5/110	5/110	5/93	5/113	5/90
Standard deviation ($\sigma(Z)$)		0.032	0.035	0.032	0.040	0.029	0.027
$-\log[H^+]$ range		3.4–7.3	3.0–6.7	3.5–9.5	3.5–10.5	2.3–11.0	2.3–8.5

values for the β_{pqr} constants of the complex species formed for each cation, defined by means of the equilibria

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

the formation constants K (species $[MHL]^-$ and $[ML]^{2-}$) and ionization constants K_i (species $[MHL]^-$), could readily be determined (Table I).

In the calculations performed by means of the LETAGROP program the values used were those of the ionization constants K_i of the 4-Cl-*o*-PDTA acid given in Ref. 2. In analogous calculations with the MINIQUAD program, the values used were those obtained in this work: $pK_1 = 3.30$; $pK_2 = 3.73$; $pK_3 = 4.85$; $pK_4 = 5.96$.

For comparison, data reported in the literature for values of log K for alkaline earth complexes of *o*-PDTA,[4] (*o*-PDTA = *ortho*-phenylenediamine-*N,N,N',N'*-tetraacetic acid), 3,4-TDTA[4] (3,4-TDTA = 3,4-toluenediamine-*N,N,N',N'*-tetraacetic acid) and EDTA[5] (EDTA = ethylenediamine-*N,N,N',N'*-tetraacetic acid) are given in Table II, as well as those for beryllium(II) with the same acids.[1] The values of log K (Table II), which follows the order EDTA > 3,4-TDTA > *o*-PDTA > 4-Cl-*o*-PDTA, can be explained by considering the basicities (nitrogen) of the ligands.[1] The formation of the same types of complex species by EDTA and by the three diaminetetramethylcarboxylic ligands derived from aromatic diamines in an *ortho* position is due to the fact that they all possess a comparable conformation with respect to the nitrogen atoms.[1,2] EDTA, 3,4-TDTA, *o*-PDTA and 4-Cl-*o*-PDTA acids are appropiate ligands for the coordination of the alkaline earth cations classed in the so-called "irregular" sequence,[6] *i.e.*, Be(II) < Ca(II) > Mg(II) > Sr(II) > Ba(II), thus explaining the greater stability of the $[CaL]^{2-}$ complexes with respect to $[BeL]^{2-}$. These ligands are potentially hexadentate and totally fulfil the coordination needs of the hexacoordinate and larger cation Ca^{2+}, by forming two new five-membered chelate rings (beryllium(II) is tetracoordinate[1]).

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TABLE II
Stability constants (log K) for the complexes $[ML]^{2-}$ of 4-Cl-*o*-PDTA, *o*-PDTA, 3,4-TDTA and EDTA acids with beryllium(II), magnesium(II), calcium(II), strontium(II) and barium(II).

LIGAND	Be(II)	Mg(II)	Ca(II)	Sr(II)	Ba(II)
4-Cl-*o*-PDTA	5.79[a]	6.16[b]	8.17[b]	5.53[b]	4.21[b]
o-PDTA	6.51[a]	6.84[c]	8.60[c]	6.22[c]	4.85[c]
3,4-TDTA	6.88[a]	7.38[c]	9.26[c]	6.59[c]	5.11[c]
EDTA	8.06[a]	8.83[d]	10.61[d]	8.68[d]	7.80[d]

[a] Ref. [1] (25°C; I = 0.5 M in $NaClO_4$). [b] This work (MINIQUAD program, Table I). [c] Ref. [4] (25°C; I = 0.1 M in KCl). [d] Ref. [5] (25°C; I = 0.1 M).

For the same ligands with zinc(II) and cadmium(II), values of log K for the species $[ML]^{2-}$ are compared in Table III with the corresponding values for cobalt(II), nickel(II) and copper(II). The Irving–Williams sequence Co(II) < Ni(II) < Cu(II) > Zn(II) is fulfilled. 3,4-TDTA, *o*-PDTA and 4-Cl-*o*-PDTA are strong complexing agents, although somewhat less so than with EDTA because of the lower basicity of aromatic amines with respect to aliphatic amines and because of distortions of octahedral symmetry imposed by the planar N–C–C–N structure which includes both nitrogen atoms.[2,7]

TABLE III

Stability constants (log K) for the complexes $[ML]^{2-}$ of 4-Cl-*o*-PDTA, *o*-PDTA, 3,4-TDTA and EDTA acids with zinc(II), cadmium(II), cobalt(II), nickel(II) and copper(II) (25°C; I = 0.1 M in KCl).

LIGAND	Zn(II)	Cd(II)	Co(II)	Ni(II)	Cu(II)
4-Cl-*o*-PDTA	12.35[a]	12.15[a]	12.75[b]	14.93[b]	15.15[b]
o-PDTA	12.89[c]		13.18[c]	13.48[c]	15.21[c]
3,4-TDTA					16.00[b]
EDTA	16.44[d]	16.36[d]	16.26[d]	18.52[d]	18.70[d]

[a] This work (MINIQUAD and LETAGROP programs, Table I). [b] Ref. [2]. [c] Ref. [7]. [d] Ref. [5].

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