DALTON
FULL PAPER

Crystal structure of the 3-D complex [$(H_2O)Cd(\mu$-3,4-TDTA)-$Cd(H_2O)$]. Potentiometric and ^{113}Cd NMR studies in aqueous solution (3,4-TDTA = 3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetate)

Joaquín Sanchiz,[a] Pedro Esparza,[a] Sixto Domínguez,[a] Alfredo Mederos,*[a] David Saysell,[b] Agustin Sánchez,[c] Rafael Ruano[d] and Juan Manuel Arrieta[e]

[a] *Department of Inorganic Chemistry, University of La Laguna, 38204 La Laguna, Tenerife, Canary Islands, Spain. E-mail: amederos@ull.es*
[b] *Department of Chemistry, The University of Newcastle Upon Tyne, Newcastle, UK NE1 7RU*
[c] *Department of Inorganic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, E-15706 Santiago de Compostela, Galicia, Spain*
[d] *Faculty of Natural Sciences, Salta National University, Salta, República Argentina*
[e] *Departament of Inorganic Chemistry, University of the País Vasco, Apartado 644, E-48080, Bilbao, Spain*

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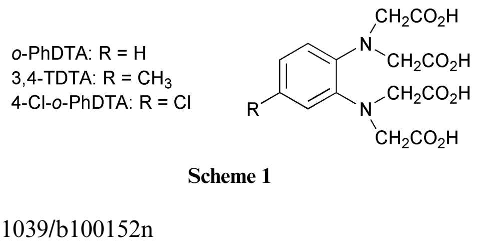
The coordinating ability of the ligands 3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (3,4-TDTA), *ortho*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (*o*-PhDTA) and 4-chloro-1,2-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (4-Cl-*o*-PhDTA) (L^{4-}) towards cadmium(II) was studied by potentiometry (25 °C, $I = 0.5$ mol dm^{-3} in $NaClO_4$) and ^{113}Cd NMR spectroscopy. The analysis of the potentiometric data showed the formation of complexes with the ligand : metal ratio 2 : 1 (identified for the first time for these ligands with any metal), $[CdH_3L_2]^{3-}$, $[CdH_2L_2]^{4-}$, $[CdHL_2]^{5-}$ and $[CdL_2]^{6-}$, with ratio 1 : 1, $[Cd(H_2L)]$, $[Cd(HL)]^-$ and $[CdL]^{2-}$, and with ratio 1 : 2, $[Cd_2H_2L]^{2+}$, and $[Cd_2L]$. The stability constants were determined. The formation of these complexes was confirmed by ^{113}Cd NMR. X-Ray diffraction structural analysis of the complex [$(H_2O)Cd(\mu$-3,4-TDTA)$Cd(H_2O)$] **1** revealed a polymeric 3-D structure in which two types of cadmium environments are produced, Cd1 and Cd2. The 3-D structure is built-up by the self-assembly of [Cd1(3,4-TDTA)]$^{2-}$ units sharing Cd2(II) ions giving interlocked infinite chains that run along the 3 directions. Cd1 is coordinated to two N atoms and four O atoms of the same ligand and one water molecule, Cd2 to six carboxylate-oxygen atoms from four different ligands and to a water molecule. The selective uptake of cadmium(II) was analyzed by means of chemical speciation diagrams as well as so-called conditional or effective formation constants $K^{\mathrm{eff}}_{\mathrm{Cd}}$. The results indicate that, in competition with other ligands that are strong complexing agents for cadmium(II), the present ligands are better sequestering agents in acidic media.

Introduction

In search of molecular based materials with interesting properties such as catalysis, clathration, *etc.* much attention has been paid to the synthesis of one-, two- and three-dimensional extended solids involving cadmium(II).[1] Rigid bridged ligands are frequently employed to construct these materials. The phenylenediaminotetraacetato ligands, such as 3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (4-methyl-*o*-phenylenedinitrilotetraacetate) (3,4-TDTA), *ortho*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (*o*-phenylenedinitrilotetraacetate) (*o*-PhDTA) and 4-chloro-1,2-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (4-chloro-*o*-phenylenedinitrilotetraacetate) (4-Cl-*o*-PhDTA) (H_4L acids), combine a rigid aromatic ring with four flexible $CH_2CO_2^-$ groups (see Scheme 1). These ligands have a rigid structure to grow high dimensionality systems, moreover the flexible $CH_2CO_2^-$ groups allow their behavior as hexadentate chelating agents forming ML complexes. Once the ML complexes have been formed the carboxylato oxygens may behave as complexing groups towards other metal ions, that may induce the formation of extended interlocked high dimensional structures. In order to explore this potential we tried to prepare complexes involving these ligands and cadmium(II). We chose cadmium(II) due to its large size and its d^{10} configuration that permits a wide variety of geometries and coordination numbers. Another aspect of cadmium(II) chemistry is its toxic character. Cadmium is highly nephrotoxic.[2–9] It has an extremely long biological half-life,[3,10] that may cause high damage. High concentrations of cadmium compounds have proven to be carcinogenic in animal experiments.[4–9]



Scheme 1

The search for sequestering agents for cadmium(II) that could be used in a wide pH range has always been a challenge for us. In previous studies[11–13] we have observed that the ligands H_4L form very stable complexes with many metal ions. In addition, these complexes are particularly stable at low pH, where other ligands do not form very stable complexes. This makes these ligands suitable as good sequestering agents in a wide pH range. In this paper we present our work in two approaches: (i) the capacity of these ligands to give high dimensional arrays and (ii) their ability as sequestering agents for cadmium(II) in a wide pH range.

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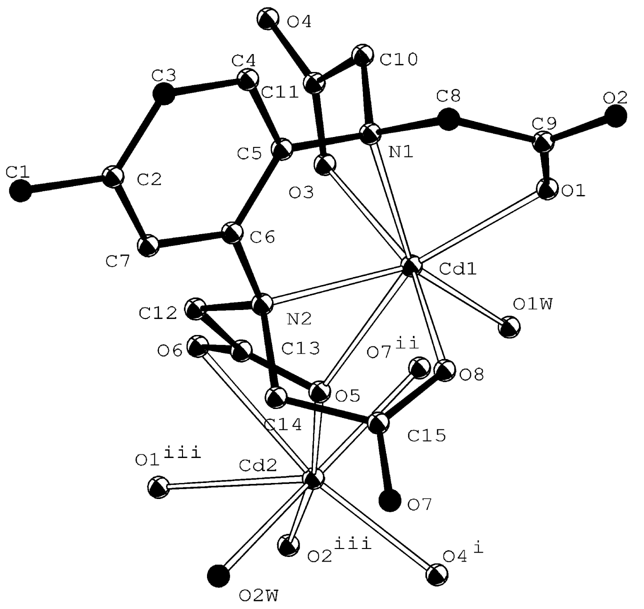

Fig. 1 ORTEP II[24] view of the compound $[(H_2O)Cd(\mu\text{-}3,4\text{-}TDTA)Cd(H_2O)]$ with labeling scheme (50% probability ellipsoids; H atoms excluded). Symmetry transformations used to generate equivalent atoms: i $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; ii $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; iii $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

Results and discussion

Crystal structure of $[(H_2O)Cd(\mu\text{-}3,4\text{-}TDTA)Cd(H_2O)]$ 1

o-PhDTA, 3,4-TDTA and 4-Cl-*o*-PhDTA are usually found to act as hexadentate ligands, however these ligands are not flexible, which gives a considerable distortion from octahedral geometry twisting towards trigonal prismatic as has been observed for complexes of Co(II),[14] Zn(II)[15] and Cu(II)[16] (with *o*-PhDTA), as well as for the cobalt(II) complex with 4-Cl-*o*-PhDTA[17] and zinc(II) complex with 3,4-TDTA.[18] Seven-coordination is found for complexes of Mg(II),[19] Mn(II)[20] and Fe(III)[21] (with *o*-PhDTA), as well as Fe(III) with 3,4-TDTA[22] and 4-Cl-*o*-PhDTA.[12] In these complexes one water molecule occupies the seventh position. In the magnesium(II) complex the molecular geometry is close to a water-capped trigonal prism, whereas the Fe(III)–3,4-TDTA and the Fe(III)–4-Cl-*o*-PhDTA complexes have a roughly pentagonal bipyramidal shape. In the $[(H_2O)_3Cd(\mu\text{-}o\text{-}PhDTA)Cd(H_2O)_2]$ complex[23] a discrete tetranuclear entity $[Cd(OH_2)]_2[Cd(OH_2)L]_2$ bridged by carboxylate-oxygen atoms is formed.

Compound **1** has a polymeric 3-D structure in which two types of cadmium environments are produced, Cd1 and Cd2 (see Fig. 1). The 3-D structure is built-up by the self-assembly of $[Cd1(3,4\text{-}TDTA)]^{2-}$ units sharing Cd2(II) ions giving interlocked infinite chains that run along the 3 directions. The chelated Cd1 is coordinated to two N atoms and four carboxylate-oxygen atoms from the ligand and a water molecule with a roughly capped trigonal prismatic environment, similar to that found in the Mg(II)–*o*-PhDTA compound.[19] The sum of the five endocyclic angles of the chelate ring of type E (pseudoethylenediamine) Cd1N1C5C6N2 is 540(1)° almost equal to that found in the chelated cadmium in the Cd_2(*o*-PhDTA) complex,[23] very similar to that found in Fe(III)–*o*-PhDTA,[21] Fe(III)–3,4-TDTA[22] and Fe(III)–4-Cl-*o*-PhDTA[12] and very close to that of an ideal pentagon. The $[Cd1(3,4\text{-}TDTA)]^{2-}$ entity acts as a complexing agent and is joined to four Cd2 atoms (see Fig. 2) in such a way that all the carboxylato-oxygens are bound to Cd atoms, which makes the ligand behave as decadentate! In this complex entity the O1C9O2 and O6C13O5 carboxylates behave as η^3-bidentate with respect to the Cd2a and Cd2 atoms, respectively. In addition O1 and O5 behave as μ-oxo bridges between cadmium ions. The O4C11O3 and O7C15O8 carboxylates act as bis(unidentate) ligands, bridging Cd1 and Cd2 in an *anti-syn* (the former) and in an *anti-anti* (the latter) conformation. The average Cd–N distance is 2.436(3) Å. The Cd1–O(carboxylate) average distance of the oxygens that act as μ-oxo bridges (O5, O1) is 2.42(9) Å, considerably longer than those of the unidentate carboxylato oxygens (O8, O3), 2.280(6) Å. The Cd–N and Cd–O(carboxylate) average distances are in between those found in the $[(H_2O)_3Cd(\mu\text{-}o\text{-}PhDTA)Cd(H_2O)_2]$ and $[(H_2O)_6\text{-}Mg(EDTA)(H_2O)Cd]_n\cdot 8H_2O$ complexes.[23,25]

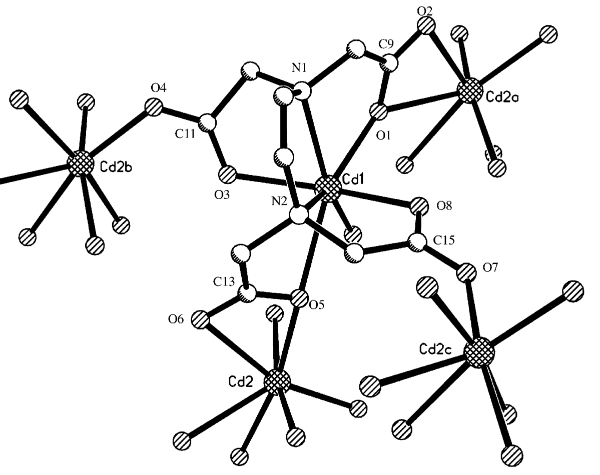

Fig. 2 View of the Cd1 environment. A part of the aromatic ring of the ligand has been omitted for clarity [symmetry transformations: Cd2a −0.5 + *x*, −0.5 − *y*, 0.5 + *z*; Cd2b −0.5 + *x*, 0.5 − *y*, −0.5 + *z*; Cd2c 0.5 + *x*, 0.5 − *y*, 0.5 + *z*].

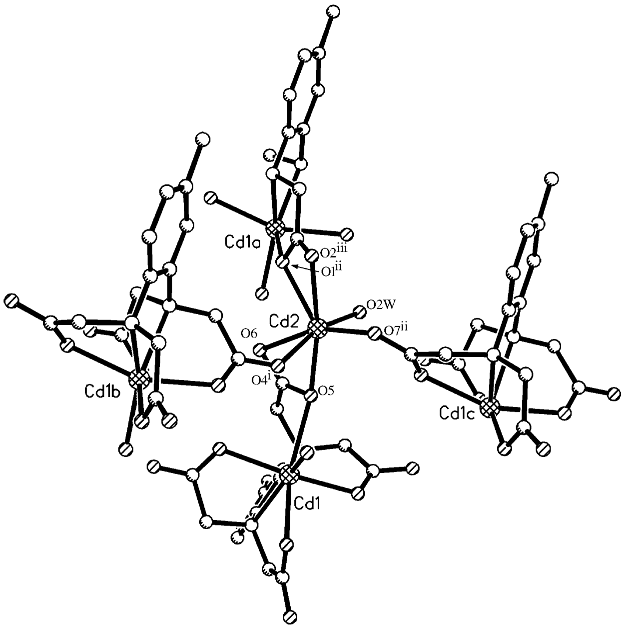

Fig. 3 View of the Cd2 environment. Symmetry transformations used to generate equivalent atoms: i $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; ii $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; iii $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; Cd1a 0.5 + *x*, 0.5 − *y*, −0.5 + *z*; Cd1b −0.5 + *x*, 0.5 − *y*, −0.5 + *z*; Cd1c 0.5 + *x*, 0.5 − *y*, 0.5 + *z*.

Cd2 has a very distorted seven coordination with an O_7 surrounding in a roughly capped trigonal prismatic environment (see Fig. 3). Six oxygen atoms from four different $[Cd1(3,4\text{-}TDTA)]^{2-}$ units and a water molecule fill its coordination sphere. Two of these complex units act as unidentate ligands joining the Cd2 atoms by an oxygen only. The other two units act as η^3-bidentate ligands with respect to the Cd2. The Cd2–O(carboxylate) distances span a wide range from 2.228(3) to 2.614(3) Å due to the very different character of the carboxylato oxygens bound to the metal (η^3 chelate, μ-oxo bridge,

Table 1 Selected bond lengths (Å) and angles (deg) for $[(H_2O)Cd(\mu\text{-}3,4\text{-TDTA})Cd(H_2O)]$

Cd1–O1W	2.226(3)	Cd1–O8	2.275(3)	Cd1–O3	2.286(3)
Cd1–O1	2.330(3)	Cd1–N2	2.436(3)	Cd1–N1	2.437(3)
Cd1–O5	2.513(3)	Cd2–O4i	2.228(3)	Cd2–O7ii	2.280(3)
Cd2–O2W	2.317(3)	Cd2–O5	2.342(3)	Cd2–O2iii	2.371(3)
Cd2–O1iii	2.543(3)	Cd2–O6	2.614(3)		
N2–Cd1–N1	72.9(1)	C5–C6–N2	121.6(3)	C6–C5–N1	120.6(3)
C5–N1–Cd1	112.3(2)	C6–N2–Cd1	112.4(2)	O1W–Cd1–O8	96.0(1)
O1W–Cd1–O3	101.9(1)	O8–Cd1–O3	158.6(1)	O1W–Cd1–O1	82.4(1)
O8–Cd1–O1	85.3(1)	O3–Cd1–O1	108.5(1)	O8–Cd1–N2	73.6(1)
O3–Cd1–N2	85.1(1)				

Symmetry transformations used to generate equivalent atoms: i $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; ii $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; iii $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

Table 2 log β_{pqr} for the complexes formed by Cd(II) with the ligands 4-Cl-*o*-PhDTA, *o*-PhDTA, and 3,4-TDTA at 25 °C, $I = 0.5$ mol dm^{-3} $NaClO_4$, compared with literature values

pqr	4-Cl-*o*-PhDTA	*o*-PhDTA	3,4-TDTA	*o*-PhDTA^a	EDTA^b
211	15.57(5)		17.65(3)		
111	14.72(2)	15.08(1)	15.53(1)	15.70	19.40
011	12.53(2)	13.00(1)	13.76(1)	13.37	16.57
312	30.19(3)	30.53(3)			
212	27.05(2)	27.40(2)	27.74(1)		
112	23.08(3)	23.35(2)	23.71(1)		
012	17.68(2)	17.35(2)	17.84(2)		
221	18.97(6)	19.63(2)	20.08(6)		
021	13.88(9)	14.62(7)	15.00(9)		
σ(E)	1.00	1.16	1.68		
ΔpH	2.0–7.1	2.0–7.0	1.9–5.8		
n	288	439	404		

^{a} 25 °C, $I = 1$ mol dm^{-3} $NaClO_4$ (ref. 27). ^{b} 25 °C, $I = 0.1$ mol dm^{-3} KNO_3 (ref. 26).

anti-anti, *anti-syn* configuration). Selected distances and angles are shown in Table 1.

Complex formation of 3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA with Cd(II)

Potentiometric studies. Taking into account the general equilibrium (1), the model and log β_{pqr} that best fit the

$$pH^+ + qCd^{2+} + rL^{4-} \rightleftharpoons [H_pCd_qL_r]^{(p+2q-4r)} \qquad \beta_{pqr} \qquad (1)$$

experimental data are shown in Table 2 and compared with the literature values for EDTA[26] and *o*-PhDTA.[27] The following order of complexation is mainly found EDTA > 3,4-TDTA > *o*-PhDTA > 4-Cl-*o*-PhDTA. The ligands 3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA show a drastic decrease in the basicity of the two nitrogen atoms, compared with EDTA, as expected from the electron-withdrawing effect, and the planarity of the benzene ring.[13] These ligands have previously been studied with other metals[13] (*o*-PhDTA[27,28] also with Cd^{2+}) and mainly monomeric ($[M(H_2L)]$, $[M(HL)]$ and $[ML]$) complexes were found. In addition to the expected $[HCdL]^-$ and $[CdL]^{2-}$ species, this is the first time that ligand rich species ($[CdL_2]^{6-}$, $[CdHL_2]^{5-}$ and $[CdH_2L_2]^{4-}$) and with excess of metal ($[Cd_2L]$ and $[Cd_2H_2L]^{2+}$) have been found in solution by potentiometric studies for these ligands. The experimental data do not converge if only 1 : 1 (ligand : metal) species are considered. Convergence is reached if the ligand rich species are also considered. As can be seen in the species distribution diagrams these species are very important in the experiments with excess of ligand (Fig. 4b).

The logic, the literature and our experience say that in solution in the $[CdL]^{2-}$ species both nitrogen atoms are coordinated to the metal ion.[14,27] The rest of the coordination positions are filled by carboxylato oxygens and water molecules with a structure similar to that found for Cd1 in **1**. Nakasuka and co-workers studied the protonation of the $[Cd(o\text{-phDTA})]^{2-}$ complex.[27,28] They concluded that in solution the carboxylato groups can be detached from the metal ion, followed by a hydration, eqn. (2) [L′ denotes a ligand with a carboxylato

$$[CdL]^{2-} + H_2O \rightleftharpoons [Cd(H_2O)L']^{2-} \qquad (2)$$

group detached from the coordination sphere of the Cd(II)]. Under these conditions the hydrated species $[Cd(H_2O)L']^{2-}$ can act as a complexing agent by joining the detached carboxylate to other metal ions and forming metal rich species. In the metal-rich species we would thus have a Cd(II) chelated by the phenylenediaminetetraacetato ligand and another Cd(II) joined to carboxylato-oxygen atoms and water molecules. The environments of the two cadmium(II) ions would be very different and so the chemical shifts of the NMR spectra. The stability constants of the stepwise complex formation would be very different too, as in the equilibria (3), log $K = 12.53$, 13.00

$$Cd^{2+} + L^{4-} \rightleftharpoons [CdL]^{2-} \qquad (3)$$

and 13.76 for 4-Cl-*o*-PhDTA, *o*-PhDTA and 3,4-TDTA, respectively (see Table 2), whereas for equilibria (4) log $K =$

$$Cd^{2+} + [Cd(H_2O)L']^{2-} \rightleftharpoons [Cd_2L'] \qquad (4)$$

2.63, 1.62 and 1.35 for 3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA, respectively. Moreover, in the experiments with excess of ligand the $[CdL]^{2-}$ and the $[Cd(H_2O)L']^{2-}$ species can react with more ligand to form species with higher ligand : metal ratio, in which the new ligands would displace water molecules or carboxylate groups already joined to the cadmium(II). The log K of these equilibria $[CdL]^{2-} + L^{4-} \rightleftharpoons [CdL_2]^{6-}$ have much lower values (4.08, 4.35 and 5.15 for 3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA, respectively) than those of the formation of the $[CdL]^{2-}$ species (see equilibrium (3) and Table 2), in agreement with the sole coordination of the carboxylato groups. If the second ligand would bind the Cd by the nitrogen atoms the log K would be much higher and the pK of the protonated complexes should be those of the carboxylato groups (p$K \approx 3.0$), but the first two pKs have a value which is very close to the first two pKs of the L^{4-} ligands (see Tables 3 and 4), where the protonation mainly occurs in the nitrogen atoms. Thus, we think that in the ligand rich species the Cd(II) will be bound to two nitrogen atoms of a ligand and the rest of the coordination positions will be filled by carboxylato oxygens from both ligands. Compared to the Cd(II) in the $[CdL]^{2-}$ species, the Cd(II) in the ligand rich species will have a very similar surrounding and therefore a similar chemical shift in the NMR spectra.

Species distribution diagrams

The species distribution diagrams as a function of pH were calculated from the values of ionization constants of the lig-

Table 3 Ionization constants of 4-Cl-*o*-PhDTA, *o*-PhDTA, 3,4-TDTA, CDTA and EDTA at 25 °C, $I = 0.5$ mol dm^{-3} NaClO$_4$

Equilibrium	4-Cl-*o*-PhDTA	*o*-PhDTA	3,4-TDTA	CDTA[a]	EDTA[a]
H_4L/H_3L^-	3.16(1)[b]	3.00(2)	2.82(2)	2.45(3)	1.68(1)
H_3L^-/H_2L^{2-}	3.65(1)	3.53(2)	3.53(1)	3.35(2)	2.48(2)
H_2L^{2-}/HL^{3-}	4.62(1)	4.61(1)	4.60(1)	5.80(1)	6.05(1)
HL^{3-}/L^{4-}	5.72(1)	6.41(1)	6.76(1)	9.31(1)	8.90(1)
σ(E)	1.50	1.61	0.91	0.95	0.98
ΔpH	2.3–8.0	2.6–7.2	3.3–10.2	2.5–10.4	2.7–10.1
n	116	95	98	94	85

[a] From ref. 11; CDTA = cyclohexane-1,2-diyldinitrilotetraacetate. [b] Values in parentheses are standard deviations.

Table 4 Deprotonation of the ligand rich species (pK_i)

	4-Cl-*o*-PhDTA	*o*-PhDTA	3,4-TDTA
$[CdL(H_3L)]^{3-} \rightleftharpoons H^+ + [CdL(H_2L)]^{4-}$	3.14	3.13	
$[CdL(H_2L)]^{4-} \rightleftharpoons H^+ + [CdL(HL)]^{5-}$	3.97	4.04	4.03
$[CdL(HL)]^{5-} \rightleftharpoons H^+ + [CdL_2]^{6-}$	5.40	6.00	5.87

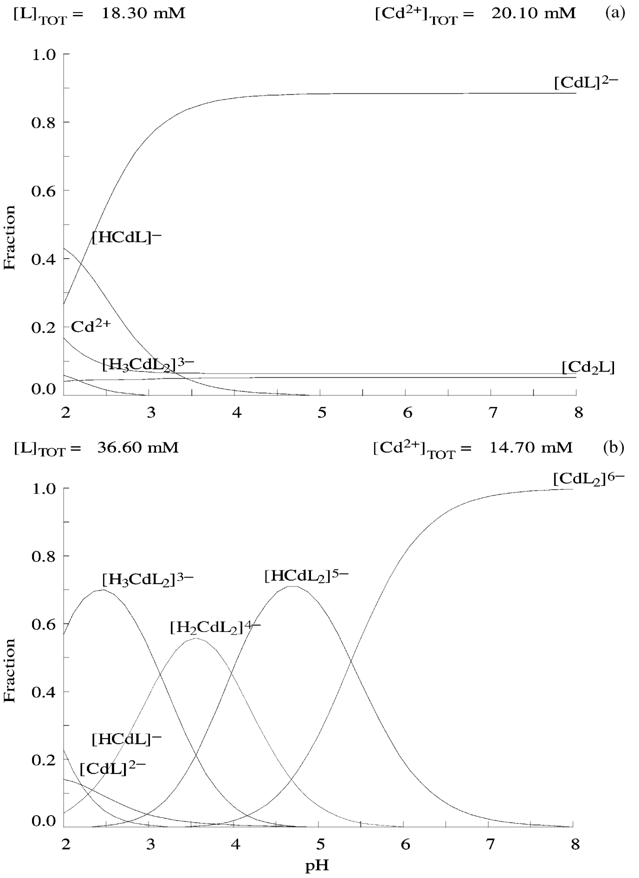

Fig. 4 Species distribution diagram as a function of pH for the Cd(II)/4-Cl-*o*-PhDTA system. (a) $[L^{4-}]_{tot} = 1.83 \times 10^{-2}$ mol dm^{-3}, $[Cd^{2+}]_{tot} = 2.01 \times 10^{-2}$ mol dm^{-3}. (b) $[L^{4-}]_{tot} = 3.66 \times 10^{-2}$ mol dm^{-3}, $[Cd^{2+}]_{tot} = 1.47 \times 10^{-2}$ mol dm^{-3}.

ands (Table 3), the log β_{pqr} of the complexes (Table 2) and the formation constants of hydrolytic species of cadmium(II).[29,30] Fig. 4(a) shows the species diagram at the ratio 1 : 1.1. The species $[Cd(HL)]^-$ is the most important at pH 2, but at pH 2.3 and higher the $[CdL]^{2-}$ species predominates. The species $[CdH_3L_2]^{3-}$ is formed in low proportion at acid pH, possibly from the reaction of $[CdL]^{2-}$ or $[Cd(HL)]^-$ with protonated species of the ligand (H_3L^- or H_4L) that are very important at these hydrogen ion concentrations. The species $[Cd_2L]$ is also formed in small, but noticeable amount and its concentration does not change very much, but is not constant in all the pH range studied. Free Cd^{2+} is also observed and its concentration decreases with the increase of the pH and remains constant above pH 3. This fact is crucial for the validation and the conclusive character of the model and the constants obtained by means of the potentiometric titrations. These ligands form very stable complexes and in these cases it is usually not possible to determine equilibria such as (3) because all the Cd(II) is bound to the ligand even at low pH. Then other techniques or competitive experiments are required.[31] In our experiments the data from experiments with excess of metal are necessary to get a result. If they are ignored the calculus does not converge. Looking carefully at the diagram for the 1 : 1.1 ratio we observe that there is a change in the free cadmium concentration in the pH range from 2 to 3, probably due to the reaction (5). This means

$$Cd^{2+} + [HCdL]^- \rightleftharpoons [Cd_2L] + H^+ \qquad (5)$$

that the concentrations of Cd(II), Cd_2L and $[HCdL]^-$ are dependent on the H^+ concentration which we are monitoring in the course of the titration. Thus, this change in the concentration of Cd(II) in the pH range 2–3 allows the SUPERQUAD[32] program to give a unique result. Similar diagrams can be drawn for the ligands 3,4-TDTA and *o*-PhDTA. At the L : M ratio 2.5 : 1 (Fig. 4b) Cd(II) is fully complexed above pH 2, and monomeric ($[Cd(HL)]^-$ and $[CdL]^{2-}$) and ligand rich species coexist. The monomeric ones exist at pH lower than 4.5, but they are minor species with respect to the ligand rich species.

The protonated species $[CdH_3L_2]^{3-}$, $[CdH_2L_2]^{4-}$ and $[CdHL_2]^{5-}$ have their maximum of existence at pH corresponding to the maximum of existence of the protonated species for the ligand, H_3L^-, H_2L^{2-} and HL^{3-}, respectively. This may indicate that these species are formed by the reaction of the $[CdL]^{2-}$ species with the respective protonated forms of the ligand, following the equilibria (6), (7) and (8). The p*K* values

$$CdL^{2-} + H_3L^- \rightleftharpoons [CdL(H_3L)]^{3-} \qquad (6)$$

$$CdL^{2-} + H_2L^{2-} \rightleftharpoons [CdL(H_2L)]^{4-} \qquad (7)$$

$$CdL^{2-} + HL^{3-} \rightleftharpoons [CdL(HL)]^{5-} \qquad (8)$$

of these protonated species are very close to the p*K*s of the protonated forms of the ligands (see Tables 3 and 4). At pH above 5.5 the species $[CdL_2]^{6-}$ predominates.

NMR studies

The spectra are shown in Fig. 5(a,b). The spin of the ^{113}Cd isotopes is $\frac{1}{2}$ and they are particularly good candidates for

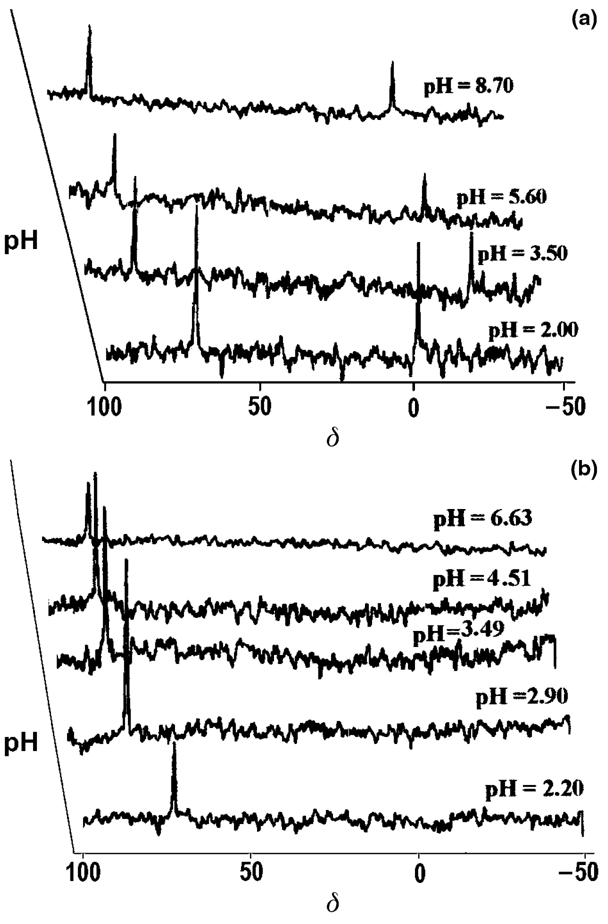

Fig. 5 ^{113}Cd NMR spectra for the Cd(II)/4-Cl-*o*-PhDTA system: (a) $[L^{4-}]_{tot} = 1.83 \times 10^{-2}$ mol dm^{-3}, $[Cd^{2+}]_{tot} = 2.01 \times 10^{-2}$ mol dm^{-3}. (b) $[L^{4-}]_{tot} = 3.66 \times 10^{-2}$ mol dm^{-3}, $[Cd^{2+}]_{tot} = 1.47 \times 10^{-2}$ mol dm^{-3}.

nuclear magnetic resonance (NMR).[33,34] The most widely utilized standard is 0.1 mol dm^{-3} aqueous $Cd(ClO_4)_2$,[33,35] probably with a $[Cd(H_2O)_6]^{2+}$ cation, which is established in the solid state crystal structures[30,35–37] as well as in aqueous solution. δ is assigned to 0 for this solution, therefore the chemical shift may be positive or negative in accordance with the type and number of ligands, as well as the geometry of the complex.[35,38] The shift depends on the number of the ligand lone-pair electrons in orbitals pointing in the direction of the metal and the ability of these ligands to donate electron pairs.[36] Thus, ligands with higher electron-donating ability than water will give positive chemical shifts, whereas those with lower will give negative ones. The shielding of ^{113}Cd(II) increases in the order O < N < S[33,39,40] and a large chemical shift range (≈1.100 ppm) can be observed.[41] Typically, substituting nitrogen for oxygen within the cadmium(II) coordination sphere tends to increase deshielding and shift the resonance downfield.

In Fig. 5(a) the ^{113}Cd spectra for the ratio ligand : metal 1 : 1.1 (ligand, 4-Cl-*o*-PhDTA) with slight excess of metal are shown. At pH 5.60 and 8.70 a shift of δ +86 is observed, similar to that found for the Cd(II)–EDTA system (δ +85.2),[33,40,42] corresponding to the $[CdL]^{2-}$ complex (see species distribution diagram, Fig. 4a). In this complex we consider that the Cd(II) is bound to two nitrogen atoms, to carboxylato oxygens and to one or various water molecules. On decreasing the pH, δ_{obs} decreases to 72, mainly due to the formation of the $[Cd(HL)]^-$ species, but also by the $[CdH_3L_2]^{3-}$ species. $[Cd(HL)]^-$ is formed by the reaction of $[CdL]^{2-}$ with H^+ and the formation of $[CdH_3L_2]^{3-}$ is described in equilibrium (6). When the complexes undergo rapid exchange in solution (on the NMR timescale) the chemical shifts of the individual species are not observed, on the other hand we have a single averaged chemical shift $\delta_{obs} = \Sigma P_i\delta_i$, where P_i and δ_i are the individual mole fraction and chemical shift, respectively.[43–45] We have taken from the spectra δ_{CdL} 86 and assume that the ligand rich species $[CdH_3L_2]^{3-}$ have a chemical shift very close to that of the $[CdL]^{2-}$ species (we will discuss this later). Then taking the individual mole fractions from the species distribution diagrams (Fig. 4a) we calculate δ_{HCdL} 61. This indicates that in the protonated complex the Cd(II) is less shielded than in the $[CdL]^{2-}$ complex. This is not surprising since the binding of the H^+ to the ligand will decrease its electron density available to be donated and to shield the Cd(II).

In addition to those resonances in the positive region others in the range 0 to −25 ppm are observed in the pH range 2.00–8.70. These chemical shifts correspond to the $[Cd(H_2O)_6]^{2+}$ ion and to the second Cd(II) in the $[Cd_2L]$ species. This Cd(II) must be bound to carboxylato groups that may have been detached from the $[CdL]^{2-}$ complex [in aqueous solution 1 M $Cd(HCO_2)_2$ and 1 M $Cd(CH_3CO_2)_2$ give δ −10.3 and −20.1, respectively[46]]. Here again due to rapid exchange we observe just one resonance for two similarly surrounded cadmium(II) ions. Other studies with ligands with carboxylic groups also gave negative chemical shifts.[36,43,47–49] The NMR spectra can be explained by the occurrence of metal rich species in which one of the metal ions is surrounded by water molecules and carboxylato oxygens (Fig. 5b). If there are no metal rich species we could not explain the occurrence of these resonances at the negative shifts.

In the spectra with excess of ligand only one signal is observed in all the pH ranges studied. In the species diagram at this concentration (Fig. 4b) we have species with 1 : 1 Cd : L ratio $[Cd(HL)]^-$, $[CdL]^{2-}$ and ligand rich species $[CdH_3L_2]^{3-}$, $[CdL(H_2L)]^{4-}$, $[CdL(HL)]^{5-}$ and $[CdL_2]^{6-}$. We have to explain how all these species have a very similar environment surrounding around Cd(II) and therefore similar or equal chemical shift. The best way (in agreement with the potentiometric studies) is to consider that in the ligand rich species one of the ligands is bound to the metal ion in a similar way as in the $[CdL]^{2-}$ complex. The second ligand will bind the Cd(II) only by the carboxylato oxygens displacing the coordinated water molecules or carboxylato groups from the ligand that were already bound to the Cd(II). Under these conditions we will have very similar environments for Cd(II) in both types of complexes and then a similar chemical shift as is observed.

Effective stability constants

The stability constants that should be used to describe the binding of metal ions to ligands are not the usual stoichiometric stability constants K_{ML} determined in aqueous solutions for simple metal–ligand equilibria, but the so-called conditional or effective binding constants,[50] which take into account the competition of the proton and other metal ions that may be present and also the competition of other ligands such as OH^-. Considering competition of H^+ to join the ligand (protonation of the ligand) and the competition of OH^- to join the metal ion (hydrolytic species of cadmium(II)), the effective formation constants K^{eff}_{ML} are related to the conventional stability constants by the expression (9). In effect, a_{CdL} takes into account

$$\log K^{eff}_{CdL} = \log K_{CdL} + \log a_{CdL} - \log a_{Cd(OH)} - \log a_L \quad (9)$$

the formation of protonated and/or ligand rich species or metal, $a_{Cd(OH)}$ is the decrease in cadmium(II) available due to its removal by the formation of hydrolytic species and a_L is the reduction of L due to the protonation of the ligand. In acidic media this is the main factor. $\log K^{eff}_{CdL}$ is a function of the pH for each ligand, and in Fig. 6 it is represented for the complexation of Cd(II) by the ligands 3,4-TDTA, *o*-PhDTA, 4-Cl-*o*-PhDTA, EDTA, octaazacryptand (1,4,7,10,13,16,24-octaazabicyclo[8.8.8]hexacosane), DMSA (2,3-disulfanylsuccinic acid) and hexacyclen (1,4,7,10,13,16-hexaazabicycloocta-

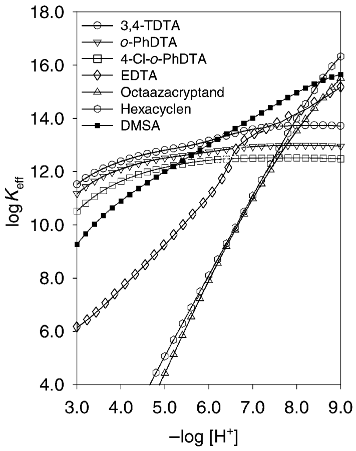

Fig. 6 Effective stability constants as a function of pH for Cd(II) with the ligands 3,4-TDTA, *o*-PhDTA, 4-Cl-*o*-PhDTA, EDTA, octaazacryptand, DMSA and hexacyclen.

decane). DMSA is a very good sequestering agent for Cd(II) and Hg(II) and it has been suggested as sequestering agent for treatment of cadmium(II) poisoning.[11–13] It is found that the ligands 4-Cl-*o*-PhDTA, *o*-PhDTA and in particular 3,4-TDTA are better sequestering agents in acidic media then the other ligands. The lower basicity of the nitrogen atoms derived from aromatic diamines facilitates chelation of Cd(II) in acidic media.[17] The effectiveness of 3,4-TDTA is only bettered by DMSA above pH 6.2 and at pH 7.4 by EDTA.

Conclusion

The ligands 3,4-TDTA, *o*-PhDTA, 4-Cl-*o*-PhDTA form very stable complexes with Cd(II). The processing of data and experience with excess of Cd(II) allowed the determination of the model and the calculation of stability constants for the equilibria. This method can be tried in the study of other systems in which strong complexes are formed. There is consistency between the potentiometric data and the ^{113}Cd NMR spectra. These ligands are not those of the highest effective constants in all the pH range studied, but they are high enough to consider them as good complexing agents in a wide pH range. In addition, 3,4-TDTA builds a very interesting 3-D structure with Cd(II).

Experimental

Materials

3,4-TDTA, *o*-PhDTA and 4-Cl-*o*-PhDTA were synthesized as previously reported.[51,52] The solutions of $Cd(ClO_4)_2$ and $NaClO_4$ were prepared by dissolving the respective salts (Merck, analytical grade) in doubly distilled water. A carbonate-free sodium hydroxide solution was prepared from an ampoule of 9959 Titrisol (Merck) and standardized against potassium hydrogenphthalate. A solution of 0.5 mol dm^{-3} $HClO_4$ was prepared by dilution of concentrated $HClO_4$ (70%, Merck) in doubly distilled water and standardized against the previously mentioned NaOH solution. Other chemicals were obtained from commercial sources and used without further purification.

emf Measurements

The H^+ ion concentrations in the equilibrium solution were measured by means of the following emf(H) cell: REF/H^+/GE; where REF (Radiometer K711 calomel) and GE (Ingold L8311) are the reference and glass electrodes, respectively. The experiments were carried out as titrations (at $I = 0.50$ mol dm^{-3} in $NaClO_4$), where the solution and the electrodes were placed in a 100 ml double-walled glass reactor vessel thermostatted at 25.0(1) °C by circulating water from a constant temperature bath. An inert CO_2-free argon atmosphere was maintained, and the solution was magnetically stirred throughout the course of the experiment. The titration was performed automatically as previously described.[12] The equilibrium was considered to be reached when the change in potential was lower than 0.1 mV in ten minutes. Treatment of emf (H^+) data was by means of the program SUPERQUAD.[32] Potentiometric titrations of the ligands in the concentration range (1.5–3.0) × 10^{-3} mol dm^{-3} and in the pH range 2.0–11.0 (pH = $-\log[H^+]$) allowed us to establish the protonation constants. The stability constants of the complexes formed were determined by processing data from potentiometric experiments performed at the following concentrations and ligand : metal ratios; 3 : 3, 3 : 2, 3 : 1, 4 : 12, 8 : 16, and 10 : 20 (× 10^{-3} mol dm^{-3}). The pH range (ΔpH) studied was 2.0–7.1. The number of experimental data processed (n) and the standard deviation of the refinement (σE) are reported in Table 2.

^{113}Cd NMR measurements

^{113}Cd NMR spectra were recorded in a Bruker AMX 500 instrument in 10 mm o.d. Wilmad tubes, using a 10 mm VSP Bruker probe. pH Adjustments were made with a Crison micro pH 2000 pHmeter. Experiments were carried out for the ligand 4-Cl-*o*-PhDTA at a concentration of 1.83 × 10^{-2} mol dm^{-3} in H_2O–D_2O 5 : 1 v/v at the ligand : metal ratios 0 : 1, 0.5 : 1, 1 : 1.1, 2.5 : 1, and 5 : 1 and in the pH range 1.8–8. A stock solution was prepared of the ligand and the acceptor, in the corresponding molar ratio, in 25 cm^3 of the solvent. The required pH values were obtained, at 25 °C, by adding drops of a very concentrated solution of NaOH or $HClO_4$. When the reading stabilized, 3 cm^3 of the solution were taken and transferred to a tube and immediately recorded at 298 K; *ca.* 15k scans were necessary to obtain peaks with a good signal : noise ratio. Chemical shifts are quoted relative to 0.1 mol dm^{-3} $Cd(ClO_4)_2$ aqueous/D_2O solution as the reference. Studies of the other ligands were also carried out, but due to the lower solubility the quality of the obtained spectra, even after a large number of scans (more than 120k), was not sufficient to reach any conclusion.

Other measurements

Thermogravimetric (TG) analyses were performed on a Netzsch STA 409 simultaneous thermobalance at a heating rate of 5 °C min^{-1} in a dinitrogen atmosphere of *ca.* 70 cm^3 min^{-1}, in the temperature range 21–700 °C. Chemical analyses (C, H and N) were performed with an EA 1108 CHNS-O automatic analyser. IR spectra (4000–450 cm^{-1}) obtained from KBr pellets were recorded with a Bruker IF S55 spectrophotometer.

Synthesis of the complex $[(H_2O)Cd(\mu\text{-}3,4\text{-TDTA})Cd(H_2O)]$ 1

$Cd(NO_3)_2$ (1.58 g, 5.1 mmol) dissolved in 10 cm^3 of water was treated with an aqueous solution (50 cm^3) of the monopotassium salt of the 3,4-TDTA acid (1.0 g, 2.54 mmol). The solution was stirred at room temperature for 15 minutes and a white precipitate was obtained (0.93 g, 60%). It was filtered off, washed with water and dried with ethanol and diethyl ether. Colorless single crystals were grown by recrystallizing the white powder from hot water. Found: C, 29.41; H, 3.05; N, 4.53. $C_{15}H_{18}Cd_2N_2O_{10}$ requires C, 29.47; H, 2.94; N, 4.58%. IR spectrum: 3420b νOH, 1620s ν_{asym}COO, 1411s cm^{-1} ν_{sym}COO. Thermal analysis: the two water molecules per formula are removed at 95 °C (theoretical 5.90%, experimental 6.10%); thermal decomposition at *ca.* 450 °C.

X-Ray diffraction analysis

The details of the structure analysis carried out on the cadmium compound are listed in Table 5. No absorption correction

Table 5 Crystal data and structural refinement parameters for [$(H_2O)Cd(\mu\text{-}3,4\text{-}TDTA)Cd(H_2O)$]

Formula	$C_{15}H_{18}N_2O_{10}Cd_2$
M	611.11
Radiation (λ/Å)	Mo-Kα, graphite monochromatized (0.71073)
Space group	Monoclinic, $P2_1/n$
a/Å	8.597(2)
b/Å	24.346(2)
c/Å	9.197(2)
β/deg	106.10(3)
Z	4
μ/cm^{-1}	23.59
T/K	100(2)
Data collected	5533
No. unique data [$I > 2\sigma(I)$]	5267
$R1$	0.0426
$wR2$	0.1307

was performed. The structure was solved by direct methods (SHELXS 86)[53] and refined with (SHELX 97).[54] Refinement was made on F^2 for all reflections. Conventional R factors are based on F, with F set to zero for negative F^2. No extinction correction was applied. The positions of the hydrogen atoms were computed and refined with an overall isotropic thermal parameter.

CCDC reference number 156000.

See http://www.rsc.org/suppdata/dt/b1/b100152n/ for crystallographic data in CIF or other electronic format.

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