

Tetramethyl Carboxylic Acids Derived from *o*-Phenylenediamines as Sequestering Agents for Iron(III): Thermodynamic Studies. X-ray Crystal Structure of Sodium Aqua(4-chloro-1,2-phenylenediamine-*N,N,N',N'*-tetraacetato)ferrate(III)–Water (1/1.5)

Joaquín Sanchiz,^{1a} Sixto Domínguez,^{1a} Alfredo Mederos,^{*,1a} Felipe Brito,^{1b} and Juan Manuel Arrieta^{1c}

Department of Inorganic Chemistry, University of La Laguna, 38204 La Laguna, Tenerife, Canary Islands, Spain; Laboratory of Equilibria in Solution, School of Chemistry, Faculty of Sciences, Central University of Venezuela, Caracas, Venezuela; and Department 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'*-tetraacetic (3,4-TDTA), *ortho*-phenylenediamine-*N,N,N',N'*-tetraacetic (*o*-PhDTA), and 4-chloro-1,2-phenylenediamine-*N,N,N',N'*-tetraacetic (4-Cl-*o*-PhDTA) acids, H₄L, with Cu(II) and Fe(III) is described. The stability constants and the partial molar enthalpies of the complexes formed (25 °C, I = 0.5 mol dm⁻³ in KNO₃) were respectively determined by means of emf and calorimetry measurements. For the system 3,4-TDTA–Fe(III) (25 °C, I = 0.5 mol dm⁻³ in NaClO₄), the stability constants of the complexes FeL⁻ and [FeL(OH)]²⁻ were also determined spectrophotometrically. The calorimetric measurements show that the complex formation is entropy driven, exothermic for Cu(II) and endothermic for Fe(III). The partial molar entropy of complexation (ΔS°) is much the same as that of the EDTA complexes. X-ray diffraction structural analysis of Na[Fe(4-Cl-*o*-PhDTA)(H₂O)]·1.5H₂O revealed that, in [FeL(OH₂)]⁻ (monoclinic *C2/c*, *a* = 10.693(3) Å, *b* = 13.931(3) Å, *c* = 24.686(6) Å, β = 94.21(2)°, *V* = 3667(2) Å³, *Z* = 8), the iron(III) is seven coordinated, with one water molecule filling the seventh position, similar to the iron(III) anionic chelates of 3,4-TDTA, *o*-PhDTA, and EDTA. The presence of the Cl atom in the aromatic ring produces an asymmetry in the Fe–N bond distances.

Introduction

The importance of iron in biological systems has been well established.^{2–4} The uptake, transport, and storage of iron in biological systems from their environment has been very thoroughly studied.^{2–7} In many cases the strategy which is employed calls upon low-molecular weight iron chelators called siderophores.^{2–10} When iron overload occurs, patients need treatment with ligands that act as sequestering agents.^{3–5,9–16} Martell *et al.*^{16,17} have prepared the hexadentate ligand *N,N*-bis(2-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid (HBED)

and other similar ligands, hexadentates or higher polydentate ligands.^{18–20} The stability constants that have been determined for such ligands are much higher than those for EDTA. Other kinds of chelating compounds utilized are similar to natural siderophores which are synthesized by microorganisms in order to take up iron from the extracellular medium.^{10–12,14,21}

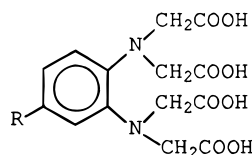
Since Fe(H₂O)₆³⁺ is readily hydrolyzed in aqueous solution at pH > 2,^{3,22–24} amino polycarboxylates such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA) are relatively ineffective as selective chelating agents for Fe(III) because they do not prevent the precipitation of ferric hydroxide in the weakly

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Chart 1



o-PhDTA; R = H

3,4-TDTA; R = CH₃

4-Cl-*o*-PhDTA; R = Cl

alkaline range (pH 8–9).^{11,16,18} Similarly, we have found that EDTA and similar ligands^{25,26} are not good sequestering agents for beryllium(II), another cation with strong hydrolysis.^{25–28} Besides, *o*-phenylenediamine-*N,N,N',N'*-tetraacetic (*o*-PhDTA), 3,4-toluenediamine-*N,N,N',N'*-tetraacetic (3,4-TDTA), and 4-chloro-*o*-phenylenediamine-*N,N,N',N'*-tetraacetic (4-Cl-*o*-PhDTA) acids (Chart 1) are hexadentate ligands derived from aromatic diamines: The lesser basicity of the nitrogen donors allows Be²⁺ to compete favorably with H⁺, to form the complex BeL₂[–] (ligands H₄L) at pH < 4, hindering the formation of the hydrolytic species of Be(II). Therefore, *o*-PhDTA, 3,4-TDTA, and 4-Cl-*o*-PhDTA are better sequestering agents for Be(II) than EDTA and similar ligands.^{25,26} This has prompted our study of ligands derived from aromatic diamines to obtain selective chelating agents for Fe(III). We report herein on the chelating ability of *o*-PhDTA, 3,4-TDTA, and 4-Cl-*o*-PhDTA with iron(III) in aqueous solution, with a view to comparing them by speciation studies not only with EDTA but also with effective sequestering agents for iron(III) studied by Martell *et al.*^{10,16–20}

Experimental Section

Materials and Solutions. 3,4-TDTA, *o*-PhDTA, and 4-Cl-*o*-PhDTA were synthesized as previously reported.^{29,30} The solutions of HNO₃, HClO₄, Fe(NO₃)₃, Cu(NO₃)₂, KNO₃, and NaClO₄ were prepared by dissolving the respective acid and salts (Merck, analytical grade) in doubly glass-distilled water which had been boiled in order to remove dissolved CO₂. To avoid hydrolysis the solution of Fe(NO₃)₃ was lightly acidified with known amounts of HNO₃ or HClO₄. A carbonate-free sodium hydroxide solution was prepared from an ampule of Titrisol Merck and standardized against potassium hydrogen phthalate. The emf and calorimetric measurements were carried out in aqueous solution at ionic strength 0.5 mol dm^{–3} in KNO₃, and spectrophotometric measurements at 0.5 mol dm^{–3} in NaClO₄.

EMF Measurements. The H⁺ and Cu²⁺ free ion concentrations in the equilibrium solution were measured by means of the following emf(H) and emf(Cu) cells: REF//H⁺/GE and REF//Cu²⁺/CuSE, where REF (Radiometer K711 calomel), GE (Ingold L8311), and CuSE (Radiometer F111 Cu-Selective) are the reference, glass, and Cu(II) selective electrodes, respectively. The experiments were carried out as titrations, where the solution **S** and the electrode(s) were placed in a 100 mL double-walled glass reactor vessel thermostated at 25.0(1) °C by circulating water from a constant temperature bath.^{31,32} An inert CO₂-free argon atmosphere was maintained, and the solution was magneti-

cally stirred throughout the course of the experiment. The titrant **T** was delivered to the equilibrium solution **S** through an immersed capillary tip from a Crison Microbur 2031 piston buret. A BASIC program³³ was used to monitor each titration point, the emf values, and the volume of solution **T** added; when the emf potential did not change more than 0.1 mV in 10 min, its value was recorded and the next volume of **T** automatically added. The cycle was repeated until the predefined total volume of **T** had been added. In an ionic medium of high concentration at 25 °C the emf potentials *E* and *E'* (mV) of the above cells follow the Nernst equation:^{34,35} $E = E^{\circ}_{\text{H}} + J[\text{H}^+] - 59.16 \text{ pH}$ and $E' = E^{\circ}_{\text{Cu}} + J[\text{H}^+] + 29.58 \log [\text{Cu}^{2+}]$, respectively, where $\text{pH} = -\log [\text{H}^+]$. Here E°_{H} , E°_{Cu} , and *J* are the standard potentials and the liquid-junction potential, respectively. The values of E°_{H} and *J*, as well as the water dissociation constant *K_w*, were determined using the Gran method by titration of a HNO₃ against NaOH.^{31–34} It was found that $\text{p}K_{\text{w}} = 13.74$, in accordance with the literature.³⁶ Likewise, E°_{Cu} was determined by using solutions **S** containing known amounts of Cu²⁺ ions.³³

Measurements were taken of ligands alone in the concentration range (1.5–3.0) × 10^{–3} mol dm^{–3} in the pH range 2.0–11.0 in order to determine the protonation constants, and measurements were also taken of the ligands [*C_L* range (2.0–3.2) × 10^{–3} mol dm^{–3}] in the presence of Ca(II) ion [*C_M* range (1.0–2.8) × 10^{–3} mol dm^{–3}] to obtain stability constants of the Ca(II) complexes.

The ligand-buffer method³⁷ is applied for the determination of the complex stability constants for the [CuL]^{2–} complex by means of the buffer CaL^{2–}–Ca²⁺ at pH = 7–9 by means of emf(Cu) measurements. The ligand, Cu(II), and Ca(II) ions total concentrations were *C_L* = (5.6–8.0) × 10^{–3} mol dm^{–3}, *C_{Cu}* = (3.1–7.0) × 10^{–3} mol dm^{–3}, and *C_{Ca}* = (21.0–51.1) × 10^{–3} mol dm^{–3}, where *C_{Ca}* + *C_{Cu}* > *C_L* > *C_{Cu}*. Later on, solutions of ligands were titrated with NaOH in presence of Cu²⁺ (*C_L* = (1.4–4.0) × 10^{–3} mol dm^{–3}, *C_{Cu}* = (0.5–2.7) × 10^{–3} mol dm^{–3}; *C_L*:*C_{Cu}* = 3:3, 3:2, 3:1) using emf(H) measurements.

These data allowed us to determine the stability constants of the [H_{*p*}CuL]^{(2–*p*)–} complexes (*p* = –1, 1, 2), once the stability constant for the [CuL]^{2–} complex was known.

Finally, for the determination of the stability constants of the Fe(III) complexes, two types of potentiometric experiments using the above emf(H) cell were performed. Type 1 consisted in the titration of acid solutions of the following composition: *C_L* = (2.8–3.8) × 10^{–3} mol dm^{–3} and *C_{Fe}* = (1.0–3.5) × 10^{–3} mol dm^{–3} (*C_L*:*C_{Fe}* = 1:1, 3:1) at pH = 2–10. Type 2 consisted in the titration of acid solutions containing ligand, Fe(III), and Cu(II) of the following composition: *C_L* = (1.3–3.5) × 10^{–3} mol dm^{–3}, *C_{Fe}* = (0.9–3.4) × 10^{–3} mol dm^{–3}, and *C_{Cu}* = (0.6–3.0) × 10^{–3} mol dm^{–3} (*C_{Fe}* + *C_{Cu}* > *C_L* > *C_{Fe}*) at pH = 2–6.

Treatment of emf (H) data was carried out by using SUPERQUAD³⁸ and the NERNST version³⁹ of LETAGROP⁴⁰ for the Cu(II), Fe(III), and Fe(III)–Cu(II)–ligand systems.

Multiwavelength Spectrophotometric Measurements of the System H⁺–Fe(III)–3,4-TDTA. UV–vis absorption spectra as a function of pH were measured in 0.5 mol dm^{–3} NaClO₄ at 25 °C, on a Shimadzu UV-2101PC spectrophotometer, whose work flow 10.0 mm quartz cuvette was connected via Teflon tubing and a peristaltic pump to the reactor-vessel containing the emf(H) cell and whose

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Table 1. Crystal Data and Structural Refinement Parameters for $\{\text{Na}[\text{Fe}(\text{OH}_2)(4\text{-Cl-}o\text{-PhDTA})]\} \cdot 1.5\text{H}_2\text{O}$

chem formula	$[\text{Na}(\text{Fe}(\text{C}_{14}\text{H}_{11}\text{ClN}_2\text{O}_8)\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$	$D_{\text{calcd}}, \text{g} \cdot \text{cm}^{-3}$	1.791
fw	494.58	$D_{\text{obsd}}, \text{g} \cdot \text{cm}^{-3}$	1.80
radiation (λ , Å)	Mo K α , graph monochrom (0.710 69)	μ, cm^{-1}	10.55
space group	monoclinic, <i>C2/c</i>	temp, °C	20
<i>a</i> , Å	10.693(3)	θ range, deg	1.65–30.15
<i>b</i> , Å	13.931(3)	data colld	6742
<i>c</i> , Å	24.686(6)	no. of unique data [$I \geq 2\sigma(I)$]	3844
<i>V</i> , Å ³	3667(2)	$R1^a$	0.0704
β , (deg)	94.21(2)	$wR2^b$	0.2019
<i>Z</i>	8		

^a $R1 = (1/r)\sum|F_o - F_c|/(1/r)\sum F_o$. ^b $wR2 = (1/r)\sum[w(F_o^2 - F_c^2)^2]/(1/r)\sum[w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (0.1386P)^2 + 13.7675P]$; $P = [\max(F_o)^2 + 2F_o^2]/3$.

reference 10.0 mm quartz cuvette contained 0.5 mol dm⁻³ NaClO₄. We used 0.5 mol dm⁻³ NaClO₄ as ionic medium instead of 0.5 mol dm⁻³ KNO₃ because of the strong absorption of the last medium at ultraviolet frequencies. Solutions of complex [FeL]⁻ and NaOH of the compositions **S** = [FeL]⁻, 0.05 × 10⁻³ mol dm⁻³ in 0.5 mol dm⁻³ NaClO₄, and **T** = NaOH, 0.200 mol dm⁻³ in 0.5 mol dm⁻³ NaClO₄, respectively, were prepared. The UV–vis experiments were made by titration of the solution **S** kept in the reactor vessel and circulating through the spectrophotometer *work flow* cuvette by means of the peristaltic pump, with known amounts of solution **T** successively added from an automatic microburet, while monitoring the absorbance D_{kj} of the *k*th solution at the *j*th wavelength versus pH.⁴¹ Spectra were recorded after attainment of constant absorbance readings. Around 800 points were measured for the pH values 5.64, 7.70, 8.25, 8.62, and 9.13, from which one set of 120 points was treated at 24 wavelengths in the range 215 ≤ λ ≤ 315 nm.

Computations of the UV–vis data were made using the Coleman isobestic point treatment⁴² and the version SPEFO⁴³ of LETAGROP.⁴⁰

Calorimetric Measurements. Enthalpy measurements were made in a precision titration calorimeter described elsewhere,^{44–47} in a solution **S** at 0.5 mol dm⁻³ in KNO₃ as ionic medium, and thermally equilibrated at 25.000(1) °C. The calorimeter was calibrated by titrating a 0.020 mol dm⁻³ NaOH with a 0.150 mol dm⁻³ HNO₃. The resulting heat of neutralization was found to be $\Delta H^\circ = -56.45(8)$ kJ mol⁻¹. This value agrees very well with the literature value³⁶ ($\Delta H^\circ = -56.4$ kJ mol⁻¹). For the determination of the heat of ligand protonation, the experiments were performed by titration of ligand **C**_L = (12.7–18.2) × 10⁻³ mol dm⁻³ at pH ≈ 7 with 0.150 mol dm⁻³ HNO₃. Likewise, for the determination of the relative molar enthalpy⁴⁸ of the Cu(II) complexes, the solution **S** of ligand with **C**_L = (10.4–13.7) × 10⁻³ mol dm⁻³ at pH ≈ 7 was titrated with a solution **T** of Cu(NO₃)₂ with **C**_{Cu} = 0.156 mol dm⁻³. Finally, for the determination of the partial molar enthalpy of the Fe(III) complexes, the experiments were carried out by titration of the solution **S** of ligand, with **C**_L = (12.8–18.4) × 10⁻³ mol dm⁻³ at pH ≈ 4, and solution **T** of Fe(NO₃)₃, with **C**_{Fe} = 0.144 mol dm⁻³ and 0.025 mol dm⁻³ in HNO₃.

Analysis of the calorimetric data was carried out using the version KALLE⁴⁹ of LETAGROP.⁴⁰

Preparation of the Complex $\text{Na}[\text{Fe}(4\text{-Cl-}o\text{-PhDTA})(\text{OH}_2)] \cdot 1.5\text{H}_2\text{O}$.

The sodium salt of the Fe(III)–4-Cl-*o*-PhDTA complex was prepared by mixing equimolecular amounts (1.0 × 10⁻³ mol) of aqueous solutions of iron(III) nitrate and 4-Cl-*o*-PhDTA. The final pH was adjusted to 4.5 by the addition of 0.1 mol dm⁻³ NaOH. Addition of 2-propanol to the solution resulted in a polycrystalline precipitate. Crystals suitable for X-ray crystallography were grown by liquid-vapor diffusion, using water as solvent and 2-propanol as precipitant. Anal. Found for the crystal: C, 33.84; N, 5.72; H, 3.30; Na, 4.90. Calcd for C₁₄H₁₆N₂O_{10.5}FeNa: C, 34.00; N, 5.66; H, 3.26; Na, 4.65. Elemental analyses were performed on a Carlo Erba 1106 automatic analyzer. Na was determined by atomic absorption.

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements were carried out for the solid-state complexes in the temperature range 80–300 K with a fully automatized AZTEC DSM8 pendulum-type susceptometer equipped with TBT continuous-flow cryostat and a Bruker BE15 electromagnet operating at 1.8 T. The apparatus was calibrated with HgCo(NCS)₄. For the Fe(III)–4-Cl-*o*-PhDTA complex, in all of the temperature range studied a high-spin complex was found with $\mu_{\text{eff}} = 5.88 \mu_{\text{B}}$. The Fe(III)–3,4-TDTA

complex, the structure of which was described in a previous work,⁵⁰ shows a similar behavior.

X-ray Structure Analysis. Many of the details of the structure analysis carried out on the iron compound are listed in Table 1. Intensity data for an orange prismatic crystal with dimensions 0.8 × 0.6 × 0.3 mm were measured using a Nonius CAD-4 diffractometer. Graphite-monochromated Mo K α radiation ($\lambda = 0.710 69$ Å) was used as the X-ray source. The $\omega/2\theta$ scan technique was employed to measure the intensities for 6742 reflections up to a maximum value of $\theta = 30.15^\circ$, $R_{\text{int}} = 0.072$, and $0 \leq h \leq 15$, $0 \leq k \leq 19$, and $-34 \leq l \leq 34$. Cell dimensions were determined from 25 centered reflections ($3 \leq \theta \leq 30^\circ$). An empirical correction for absorption (DIFABS)⁵¹ was applied (maximum 0.949 and minimum 0.869). The structure was solved by direct methods (SHELX-86)⁵² and refined with (SHELX-93).⁵³ Refinement was made on F^2 for all reflections except for those with very negative F^2 or flagged by the user for potential systematic errors. Weighted R -factors wR and all goodnesses of fit S are based on F^2 ; conventional R -factors R are based on F , with F set to zero for negative F^2 . The observed criterion of $F_o > 4\sigma(F_o)$ is used only for calculating the observed R factor, etc., and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R factors based on all data will be even larger. Reflections were weighted according to the formula $w = 1/[\sigma^2(F_o^2) + (0.1386P)^2 + 13.7567P]$, where $P = (F_o^2 + 2F_c^2)/3$. No extinction correction was applied. The hydrogen atoms of the ring were positioned in ideal positions and refined with an overall isotropic temperature factor. The hydrogen atoms of the hydrocarbon chain were positioned in ideal positions and refined with a second overall isotropic temperature factor. The hydrogen atoms of the water molecule were located from a Fourier difference map and imposed in fixed positions in the last cycles of refinement with a third overall isotropic temperature factor. Table 2 reports selected bond lengths and angles. Other crystallographic data are summarized in Tables S1–S5 of the Supporting Information.

Results and Discussion

Crystal Structure. The determination by X-ray diffraction of the structure of the complex $[\text{Fe}(\text{OH}_2)(o\text{-PhDTA})]^-$ solved

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Na}[\text{Fe}(\text{OH}_2)(4\text{-Cl-}o\text{-PhDTA})]] \cdot 1.5\text{H}_2\text{O}$

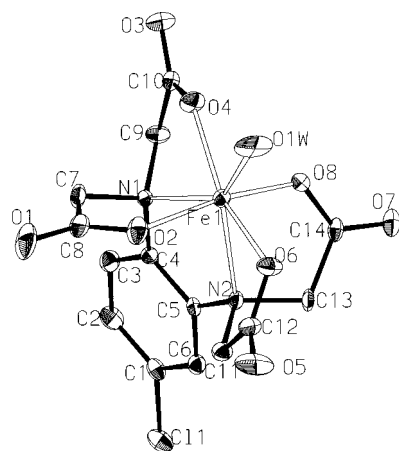
(a) Coordination Sphere of Iron					
Fe1—O2	1.980(3)	Fe1—O8	1.983(3)	Fe1—O4	2.023(3)
Fe1—O6	2.070(3)	Fe1—O1W	2.080(3)	Fe1—N1	2.321(3)
Fe1—N2	2.341(3)				
O2—Fe1—O8	165.9(1)	O2—Fe1—O4	97.3(1)		
O2—Fe1—O6	85.5(1)	O2—Fe1—O1W	94.2(2)		
O2—Fe1—N1	76.3(1)	O2—Fe1—N2	91.4(1)		
O8—Fe1—O4	89.3(1)	O8—Fe1—O6	95.7(1)		
O8—Fe1—O1W	99.6(1)	O8—Fe1—N1	93.9(1)		
O8—Fe1—N2	75.8(1)	O4—Fe1—O6	147.4(1)		
O4—Fe1—O6	147.4(1)	O4—Fe1—O1W	75.0(1)		
O4—Fe1—N1	72.4(1)	O4—Fe1—N2	141.7(1)		
O6—Fe1—O1W	72.4(1)	O6—Fe1—N1	138.9(1)		
O6—Fe1—N2	70.3(1)	O1W—Fe1—N1	144.5(1)		
O1W—Fe1—N2	141.6(1)	N1—Fe1—N2	73.6(1)		

(b) Calculated Planes (deg) of the "Glycine" Chelate Rings

type	planes	4-Cl- <i>o</i> -PhDTA av	3,4-TDTA ^a av
R	Fe1N1C7C8O2 and Fe1N2C13C14O8	532(1)	533(1)
G	Fe1N1C9C10O4 and Fe1N2C11C12O6	520(1)	522(1)

(c) Fe—O Distances (Å) in Both Type R and Type G Rings and Fe—OW Distances (Å) for the Fe(III) Complexes

	4-Cl- <i>o</i> -PhDTA	3,4-TDTA ^a	<i>o</i> -PhDTA ^b	EDTA ^c
type R	1.981(3)	1.975(3)	1.990	1.969
type G	2.047(3)	2.062(3)	2.067	2.119
Fe—OW	2.080(3)	2.101(3)	2.057	2.107

^a Reference 50. ^b Reference 54. ^c Reference 56.**Figure 1.** ORTEP view of the $[\text{Fe}(\text{OH}_2)(4\text{-Cl-}o\text{-PhDTA})]^-$ anionic chelate complex (50% probability ellipsoids; H atom excluded).

by Mizuno *et al.*⁵⁴ shows that Fe(III) is heptacoordinated, with a roughly bipyramidal-pentagonal geometry and C_{2v} symmetry. The two Fe—N bonds are equal (2.344(3) Å), as expected. In the complex $[\text{Fe}(\text{OH}_2)(4\text{-Cl-}o\text{-PhDTA})]^-$ (Figure 1) the introduction of a Cl atom into the aromatic ring in position 3 produces the loss of the C_{2v} symmetry, and it is to be expected that the Fe—N bonds with the N atom in a *para* position and with the N atom in a *meta* position are different (Table 2). This fact has been seen in the complex $[\text{Fe}(\text{OH}_2)(3,4\text{-TDTA})]^-$, previously described,⁵⁰ where the introduction of a methyl group in position 3 produces the same effect in the symmetry of the complex. The Fe—N bond lengths in the complexes $[\text{Fe}(\text{OH}_2)(4\text{-Cl-}o\text{-PhDTA})]^-$ (Table 2) and $[\text{Fe}(\text{OH}_2)(3,4\text{-TDTA})]^-$ ⁵⁰ with the N atom in a *meta* position are practically equal. On the

(54) Mizuno, M.; Funahashi, S.; Nakasuka, N.; Tanaka, M. *Inorg. Chem.* **1991**, *30*, 1550.**Table 3.** Ionization Constants ($\text{p}K_i$) of 4-Cl-*o*-PhDTA, *o*-PhDTA, 3,4-TDTA, CyDTA, and EDTA (25 °C; $I = 0.5 \text{ mol dm}^{-3}$ in KNO_3)

equilibria	4-Cl- <i>o</i> -PhDTA	<i>o</i> -PhDTA	3,4-TDTA	CyDTA ^a	EDTA ^a
$\text{H}_4\text{L}/\text{H}_3\text{L}^-$	3.23(1) ^b	2.99(2)	2.80(2)	2.42	2.00
$\text{H}_3\text{L}^-/\text{H}_2\text{L}^{2-}$	3.64(1)	3.50(2)	3.51(1)	3.53	2.69
$\text{H}_2\text{L}^{2-}/\text{HL}^{3-}$	4.66(1)	4.61(1)	4.65(1)	6.15	6.13
$\text{HL}^{3-}/\text{L}^{4-}$	5.79(1)	6.41(1)	6.80(1)	12.4	10.19
$\sigma(E)$	1.70	1.41	0.61		
ΔpH	2.3–8.0	2.6–7.2	3.3–10.2		
n	106	90	92		

^a From ref 36. ^b Values in parentheses are standard deviations.

other hand, the length in the *para* position is shorter in the $[\text{Fe}(\text{OH}_2)(3,4\text{-TDTA})]^-$ complex due to the higher electron-donor effect exhibited by the methyl radical in this position.⁵⁵ The comparison of the Fe—N bond lengths of 4-Cl-*o*-PhDTA (Table 2), *o*-PhDTA,⁵⁴ and 3,4-TDTA⁵⁰ with those of EDTA⁵⁶ (2.325 Å) and CyDTA⁵⁷ (2.290 Å) shows longer distances for ligands derived from aromatic diamines, as expected by the electron-withdrawing effect of the benzene ring. A similar effect for the stability constants of the Fe(III) complexes is observed (Table 4).

The $[\text{Fe}(\text{OH}_2)(4\text{-Cl-}o\text{-PhDTA})]^-$ complex (Figure 1) is seven-coordinate with 4-Cl-*o*-PhDTA⁴⁻ as a hexadentate ligand and one water molecule filling the seventh position, similar to the anionic iron(III) chelates of *o*-PhDTA,⁵⁴ 3,4-TDTA,⁵⁰ EDTA,⁵⁶ and of CyDTA.⁵⁷ The complex has a roughly pentagonal-bipyramidal shape, as has been observed in most Fe(III)—EDTA complexes,⁵⁶ in the Fe(III)—3,4-TDTA⁵⁰ complex, and in the Fe(III)—*o*-PhDTA complex.⁵⁴ In these cases each Fe(III) ion occupies the center of a bipyramid; thus, Fe1 (Figure 1) occupies the center of the pentagonal equatorial plane whose vertices are O4, O6, O1W, N1, and N2, the deviations from the ideal plane of these atoms (in Å) being O4 −0.240, O6 0.212, O1W 0.044, N1 0.307, and N2 −0.279. O2 and O8 occupy the apical positions. The sum of the five angles around the central Fe1 ion is 363.7(5)° (364.1(5)° in the Fe(III)—3,4-TDTA complex;⁵⁰ 362.9(2)° in the Fe(III)—*o*-PhDTA complex⁵⁴). The sum of the five endocyclic angles of the chelate ring of type E (pseudo-ethylenediamine) Fe1N1C4C5N2 is 540(1)° (equal to that corresponding to the Fe(III)—3,4-TDTA complex⁵⁰), very close to that of an ideal pentagon, 540°, and considerably greater than that of the chelate ring in Fe(III)—CyDTA, 518.7°,⁵⁷ and Fe(III)—EDTA.⁵⁶

The planes of the "glycine" chelate rings Fe—O—C—C—N have been calculated and classified according to Hoard's proposal⁵⁸ (Table 2).

The NaO_6 polyhedron may be described as a distorted octahedron. The Na—O distances are listed in Table S3, showing a mean distance of 2.518 Å and a range of 2.758(3)—2.377(4) Å. The O(3W) atom bridges two Na⁺ ions (Figure S1).

Ionization Constants of the Acids. The ionization constants of the acids K_i were calculated with SUPERQUAD,³⁸ and the results are given in Table 3, compared with the values reported for EDTA and CyDTA.³⁶ The values found for $\text{p}K_i$ are in good

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Table 4. Stability Constants (log *K*) of the Complexes of Ca(II), Cu(II), and Fe(III) (25 °C; *I* = 0.5 mol dm⁻³ in KNO₃)

equilibria	4-Cl- <i>o</i> -PhDTA	<i>o</i> -PhDTA	3,4-TDTA	EDTA ^a
Ca ²⁺ + HL ³⁻ /[CaHL] ⁻	4.82(2) ^b	4.82(2)	4.77(2)	
Ca ²⁺ + L ⁴⁻ /[CaL] ²⁻	7.71(1)	8.23(1)	8.61(1)	
$\sigma(E)$	1.35	1.85	1.87	
$\Delta p[H]$	3.0–7.1	2.7–9.7	3.1–9.9	
<i>n</i>	73	80	127	
Cu ²⁺ + H ₂ L ²⁻ /[CuH ₂ L]	8.76(2)	8.87(2)	8.95(2)	8.9
Cu ²⁺ + HL ³⁻ /[CuHL] ⁻	11.66(2)	11.75(2)	11.73(2)	11.80
Cu ²⁺ + L ⁴⁻ /[CuL] ²⁻	14.40(2)	15.15(2)	15.57(2)	18.80
Cu ²⁺ + L ⁴⁻ + OH ⁻ /[CuL(OH)] ³⁻	17.41(3)	17.61(2)		17.7
$\sigma(E)$	2.20	1.28	1.51	
$\Delta p[H]$	1.9–8.0	2.0–8.4	3.3–8.2	
<i>n</i>	101	167	101	
Fe ³⁺ + HL ³⁻ /[FeHL]	16.30(5)	16.45(5)	16.57(5)	16.1
Fe ³⁺ + L ⁴⁻ /[FeL] ⁻	20.99(5)	21.82(5)	22.05(5), 21.57(7) ^c	25.0
Fe ³⁺ + L ⁴⁻ + OH ⁻ /[FeL(OH)] ²⁻	26.69(5)	26.98(5)	27.16(5), 27.14(4) ^c	31.5
$\sigma(E)$	2.31	1.77	3.55, 0.002 ^d	
<i>n</i>	146	197	156, 24 ^e	
$\Delta p[H]$	1.84–8.42	2.10–9.20	1.86–8.92, 5.64–9.13 ^f	
	4-Cl- <i>o</i> -PhDTA	<i>o</i> -PhDTA ^h	3,4-TDTA	
p <i>K</i> _a , equilibrium (3) ^g	8.03	8.58	8.62	

^a From ref 36. ^b Values in parentheses are standard deviations. ^c From spectrophotometric measurements at 25 °C; *I* = 0.5 mol dm⁻³ in NaClO₄. ^d $\sigma(D)$ standard deviation in absorbance. ^e Number of wavelengths computed. ^f pH range for spectrophotometric measurements. ^g This work. ^h At 25 °C and *I* = 1 mol dm⁻³ in NaClO₄, p*K*_a = 8.30.⁵⁴

agreement with those previously determined,^{29,30} taking into account the differences in ionic media. The most basic protonations correspond to protons situated fundamentally over nitrogen atoms, while the remaining protonations mainly correspond to carboxylic protons.

Complex Formation with Cu(II) and Fe(III). Since the determination of stability constants *K*_{0ML} for Fe(III) and Cu(II) from emf(H) data is rather difficult, because the complexation of the metal ion was almost complete even at pH = 2, we used the ligand–buffer method³⁷ for the determination of the stability constant *K*_{0CuL} by means of emf(Cu) data and metal–metal competition (Cu(II) *vs* Fe(III)) for the determination of the stability constants *K*_{pFeL}, using emf(H) data. The stability constants are defined in Table 4.

(a) Copper(II) Complexes. In the ligand–buffer method we used the Ca²⁺–CaL buffer, in which the ligand concentration was kept low and practically constant. [L] is given by the relation $(C_L - C_{Cu}) / ((C_{Cu} + C_{Ca} - C_L)K_{0CaL})$, and *C*_{Cu} can be regarded as [CuL]. Then *K*_{0CuL} is obtainable from eq 1 if we

$$K_{0CuL} = K_{0CaL}(C_{Cu}(C_{Cu} + C_{Ca} - C_L) / (C_L - C_{Cu})[Cu^{2+}]) \quad (1)$$

measure [Cu²⁺] under the conditions *C*_{Cu} < *C*_L < *C*_{Cu} + *C*_{Ca} at pH = 7–9.5 (Figure S2), where the protonation of CaL²⁻ and CuL²⁻ complexes is negligible. (*K*_{0CaL} was previously calculated by emf(H) measurements, Table 4; these values are in good agreement with those previously obtained at other ionic strengths^{37a,59,60}). Once the stability constants *K*_{0CuL} are known, the protonation (*p* = 1, 2) and hydrolytic constants (*p* = -1) *K*_{pCuL} for the Cu(II) complexes were calculated from the analysis of emf(H) data by means of SUPERQUAD (Table 4). These stability constants are compared with the values found in the literature for the complexes formed by Cu(II) with *o*-PhDTA,^{37a} 4-Cl-*o*-PhDTA,⁶¹ 3,4-TDTA,⁶¹ and EDTA.³⁶ It can be seen that the values of the constants *K*_{pCuL} followed the ligand sequence



The ligands 4-Cl-*o*-PhDTA, *o*-PhDTA, and 3,4-TDTA show a drastic decrease in the basicity of two nitrogen atoms, compared with EDTA, as expected from the electron-withdrawing effect of the benzene ring. The Cu(OH)L³⁻ complex for the 3,4-TDTA ligand did not reach a high enough concentration to be determined.

(b) Iron(III) Complexes. From the analysis of the absorbance data *D*(pH) for the system H⁺-Fe(III)-3,4-TDTA in 0.5 mol dm⁻³ NaClO₄ at 25 °C in the ranges 5.64 ≤ pH ≤ 9.13 and 215 ≤ λ ≤ 315 nm by means of the Coleman isosbestic point treatment⁴² (Figure 2), taking into account the structural studies for the Fe(III)-*o*-PhDTA,⁵⁴ -3,4-TDTA,⁵⁰ and -4-Cl-*o*-PhDTA (Figure 1) complexes, which show the general formula [FeL(H₂O)]⁻ with the iron(III) seven coordinated (the ligand is hexadentate and a molecule of water occupies the seventh coordination position), we conclude that in this pH range only the species [FeL]⁻ and [Fe(OH)L]²⁻ predominate in equilibrium according to reaction 3.



In addition, by means of LETAGROP^{39,40,43,49} we obtain the stability constants log *K*_{FeL} = 21.57(7) and log *K*_{FeL(OH)} = 27.14(4) with the standard deviation $\sigma(D)$ = 0.002. From these stability constants one may get p*K*_{FeL} = 8.2(1) for equilibrium 3. Figure 2 shows the experimental absorbance data for 24 wavelengths, in the position of the best fit with the absorbance values calculated using these stability constants. Similar behavior is found for the H⁺-Fe³⁺-4-Cl-*o*-PhDTA system.³³

On the other hand, emf(H) measurements (type 1 experiments) for Fe(III)-ligands systems showed a great stability of the complexes formed against alkalis, because no decomposition of the complexes formed was observed until pH > 10. This high stability of the Fe(III) complexes only allowed us to determine limit values for the stability constants *K*_{pFeL}, as well

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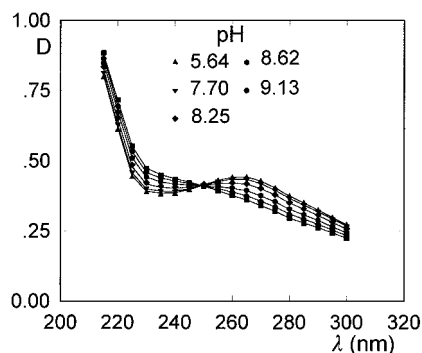


Figure 2. Experimental UV-vis spectrophotometric data for the $\text{H}^+ - \text{Fe}^{3+} - 3,4\text{-TDTA}$ system at $25\text{ }^\circ\text{C}$ and $I = 0.5\text{ mol dm}^{-3}$, in NaClO_4 at indicated pH values. The continuous-draw curves were made using the stability constants of Table 4.

as the pK values for reaction 3. This hydrolysis reaction was previously studied for the $[\text{Fe}(o\text{-PhDTA})(\text{H}_2\text{O})]^-$ complex,⁵⁴ but there were no determinations of the stability constants K_{OFeL} . Consequently, displacement methods could be required for this purpose. We used emf(H) measurements and the competition between Fe(III) and Cu(II), for instance type 2 experiments, since we know the stability constants $K_{p\text{CuL}}$ with these ligands. If an experiment is performed (type 2 experiments) in which $C_{\text{Fe}} < C_{\text{L}} < C_{\text{Fe}} + C_{\text{Cu}}$ and the titration is started at $\text{pH} \approx 2$, it is observed that at $\text{pH} > 4.5$ the equilibria takes a long time to be reached and at a $\text{pH} \approx 6.0$ insoluble hydrolytic species appear. In the ligand-buffer with excess Cu^{2+} , [L] is kept so low that the equilibrium



is much favored to the right-hand side as compared to the type 1 experiment. Subsequently, the free ligand is complexed to Cu^{2+} in excess forming the CuL^{2-} complex (see species distribution diagrams of type 2 experiments, Figure S3). If the potentiometric data from experiments type 1 and type 2 are processed with SUPERQUAD³⁸ (and also LETAGROP³⁹), taking into account the stability constants for Cu(II) complexes (known previously, Table 4) and the hydrolytic species for Cu(II)⁶² and for Fe(III),²⁴ the stability constants for Fe(III) complexes are obtained in good agreement with those obtained from the above-mentioned UV-vis study, shown in Table 4, compared with the values found for EDTA. The order of stability found is that expected similar to Cu(II), sequence (2). The values of pK_a for equilibrium 3 are also in Table 4. The species distribution diagrams as a function of $-\log[\text{H}^+]$ (Figure S4) show the large affinity of these ligands for iron(III) being fully complexed from a pH as low as 2. At low pH the protonated complex FeHL is formed and at pH higher than 6 the hydroxo complex $[\text{FeL}(\text{OH})]^{2-}$ is formed, but no insoluble hydrolytic species of Fe(III) appears until reaching a pH higher than 10, as was verified experimentally (type 1 experiments).

Thermodynamic Quantities. Emf studies have shown that the basicity of the nitrogen atoms in 3,4-TDTA, *o*-PhDTA, and 4-Cl-*o*-PhDTA is considerably weaker than that of other amino polycarboxylates such as EDTA, and the effect of a Cl atom in 4-Cl-*o*-PhDTA and the methyl group in 3,4-TDTA produces the sequence shown in (2). Thermodynamic quantities of ligand protonation from the calorimetric measurements are given in Table 5 compared to those of EDTA. The first protonation is exothermic for EDTA,³⁶ 3,4-TDTA, and *o*-PhDTA but endo-

thermic for 4-Cl-*o*-PhDTA, and the second is endothermic for 3,4-TDTA, *o*-PhDTA, and 4-Cl-*o*-PhDTA. The endothermicity confirms a decrease in the basicity because of the electron-withdrawing effect of the phenylene group observed in potentiometric measurements and the effect of the Cl atom and methyl group as was seen in potentiometric studies. Third and fourth protonations occur mainly over carboxylate groups, and these are exothermic for 4-Cl-*o*-PhDTA and *o*-PhDTA. All protonations have favorable change in entropy.

Likewise, calorimetric studies allowed the changes in enthalpy ($\Delta H_{\text{ML}}^\circ$) and entropy ($\Delta S_{\text{ML}}^\circ$) of complexation of Cu(II) and Fe(III) by the ligands 3,4-TDTA, *o*-PhDTA, and 4-Cl-*o*-PhDTA to be determined. The results are obtained by means of LETAGROP,^{39,43} and they are summarized in Table 5 and compared with those of EDTA in Figure S5. The formation of CuL^{2-} complexes is exothermic for all the systems, but the drastic decrease in the basicity for the two nitrogen atoms, compared with EDTA, provokes a decrease in the value for $\Delta H_{\text{ML}}^\circ$. Changes in entropy are largely not unaffected when the ligand is changed and remain practically constant for Fe(III) and Cu(II). Fe(III) complex formation is endothermic for 4-Cl-*o*-PhDTA and *o*-PhDTA, due to the less basic nature of these ligands. An endothermicity was found also in the complexation of lanthanoids(III) with *o*-PhDTA.^{37b} The large change in entropy is responsible for the high stability of the complexes formed by Fe(III) and outweighs the endothermicity of the complexation.

Selective Uptake of Iron(III) ions. The stability constants that should be used to describe the binding of metal ions to ligands are not the usual stability constants K_{ML} but the so-called conditional or effective binding constants,^{4,63} which take into account the competition of the proton and other metal ions that may be present and also the competition of other ligands present as OH^- . Considering the competition of H^+ to join the ligand (protonation of the ligand) and the competition of OH^- to join the metal ion (hydrolytic species of Fe(III)), the effective formation constants $K_{\text{ML}}^{\text{eff}}$ are related to the conventional stability constants by the expression

$$\log K_{\text{FeL}}^{\text{eff}} = \log K_{\text{FeL}} + \log \alpha_{\text{FeL}} - \log \alpha_{\text{Fe}(\text{OH})} - \log \alpha_{\text{L}} \quad (5)$$

where $\alpha_{\text{FeL}} = 1 + \beta_{111}[\text{L}][\text{H}^+] + \dots + \beta_{-111}K_w^{-1}[\text{L}][\text{H}^+]$, $\alpha_{\text{Fe}(\text{OH})} = 1 + \beta_{-11}[\text{H}^+] + \beta_{-21}[\text{H}^+]^2 + 2\beta_{-22}[\text{Fe}^{3+}][\text{H}^+]$, and $\alpha_{\text{L}} = 1 + \sum_{i=1}^{i=N} \beta_i^{\text{H}}[\text{H}^+]^i$.

In effect, α_{FeL} takes into account the formation of protonated and/or hydroxo complexes with the ligand L, $\alpha_{\text{Fe}(\text{OH})}$ is the reduction of the Fe(III) available due to the removal of Fe(III) by the formation of the hydrolytic species for iron(III), and α_{L} is the reduction of L due to the protonation of the ligand. $\log K_{\text{FeL}}^{\text{eff}}$ is a function of the pH for each ligand and metal ion. In Figure 3 represents the complexation of Fe(III) by the ligands HBED,¹⁸ *N,N'*-bis((3-hydroxy-6-methyl-2-pyridyl)methyl)ethylenediamine-*N,N'*-diacetic acid¹⁸ (ENDA-HP), and *N,N'*-bis((3-hydroxy-6-methyl-2-pyridyl)methyl)ethylenetriamine-*N,N,N'*-triacetic acid¹⁸ (DTTA-HP), which, as has been said by Martell *et al.*,¹⁸⁻²⁰ are effective sequestering agents for Fe(III), compared with 3,4-TDTA, *o*-PhDTA, and 4-Cl-*o*-PhDTA. It is found that, in general, the ligands *o*-PhDTA and 3,4-TDTA are better sequestering agents in acid medium (Table S6), which could be interesting from the industrial point of view. In particular, Figure S6 shows the species distribution diagrams comparing the competition of the 3,4-TDTA and HBED¹⁸ ligands for the H^+ and Fe(III) ions: It is observed that 3,4-TDTA is a better

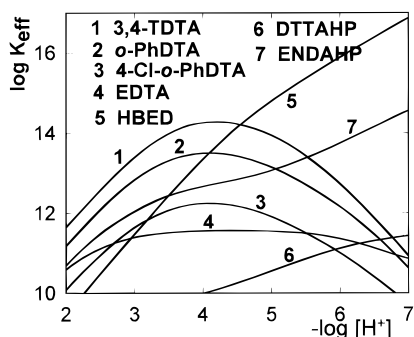
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Table 5. Thermodynamic Quantities of the Protonation of Ligands and of Complex Formation (ΔH° in kJ mol⁻¹ and ΔS° ($\times 10^{-1}$) in J mol⁻¹ K⁻¹)

	4-Cl- <i>o</i> -PhDTA		<i>o</i> -PhDTA		3,4-TDTA		EDTA ^b	
	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°
HL ³⁻	3.91(8) ^a	13.0(2)	-0.54(4)	12.89(8)	-3.82(4)	12.6(1)	-23.3(8)	11.6
H ₂ L ²⁻	2.8(1)	10.9(3)	2.64(8)	106(3)	1.96(4)	10.06(8)	-17.5(8)	5.8
H ₃ L ⁻	-5.9(2)	6.0(3)	-4.2(2)	5.74(8)	-3.7(1)	6.03(8)	5.4(4)	7.1
H ₄ L	-5.8(1)	8.1(2)	-2.03(8)	5.86(8)	1.04(8)	6.61(8)	1.2	4.16
CuL ²⁻	-3.03(8)	26.6(4)	-4.24(8)	27.4(8)	-8.4(2)	27.0(4)	-34.5	25.0
CuHL ⁻	-11.8(1)	1.83(8)	-10.2(1)	2.24(8)	-5.8(2)	3.74(8)	-8.32	2.91
CuH ₂ L	-5.8(2)	1.352(8)	-5.8(2)	1.35(1)	-9.3(3)	0.395(8)		
FeL ⁻	2.5(1)	40.8(8)	3.24(4)	42(1)	-1.7(2)	41.6(8)	-11.3	43.7
FeHL	-5.3(4)	0.29(8)	-4.2(2)	0.611(8)	0.9(2)	2.82(1)	-0.4	2.5

^a Value in parentheses are standard deviations. ^b From ref 46 for the EDTA ligand and ref 36 for the Cu(II) and Fe(III) complexes.

**Figure 3.** Effective stability constants for Fe(III) with different ligands as a function of pH.

sequestering agent at pH < 4. Similar results are obtained by comparing *o*-PhDTA and ENDA-HP. The lower basicity of the nitrogen atoms derived from aromatic diamines facilitates the chelation of iron(III) in acid medium. However, at neutral and higher pH, HBED and ENDA-HP are better sequestering agents for Fe(III) than *o*-PhDTA, 3,4-TDTA, and 4-Cl-*o*-PhDTA acids (Figures 3 and S6).

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Supporting Information Available: Listings of crystal data and structure refinement parameters, atomic coordinates and equivalent isotropic displacement parameters, complete bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters (Tables S1–S5), and effective stability constants, pH 2–10 (Table S6), and figures showing the coordination geometry of the sodium cations (Figure S1), a $-\log[\text{Cu}^{2+}]/-\log[\text{H}^+]$ diagram for determination of the stability constant of the $[\text{CuL}]^{2-}$ complex (Figure S2), a species distribution diagram calculated for the aqueous solution containing both 4-Cl-*o*-PhDTA, Cu(II), and Fe(III) simulating type 2 experiments (Figure S3) and 3,4-TDTA and Fe(III) at molar ratio 1:1 (Figure S4), the change in thermodynamic quantities in the complex formation of Fe(III) and Cu(II) with the ligands 4-Cl-*o*-PhDTA, *o*-PhDTA, 3,4-TDTA, and EDTA (Figure S5), and a species distribution diagram calculated for the aqueous solution containing 3,4-TDTA (H₄L), HBED (H₄Y), and Fe(III) (Figure S6) with captions included (14 pages). Ordering information is given on any current masthead page.

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