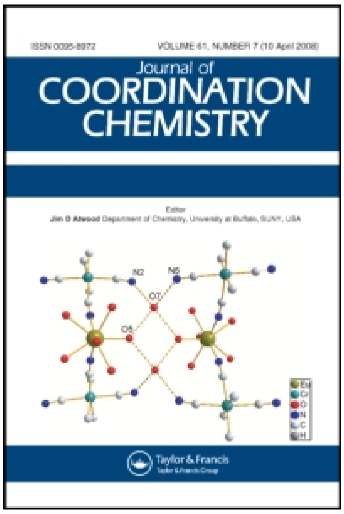

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FITTING AN UNUSUAL COMPLEXATION MODEL IN AQUEOUS ACID SOLUTIONS OF NICKEL(II) AND *N,N,N',N',-TETRAKIS*(CARBOXYMETHYL)-*L*-ORNITHINE

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FITTING AN UNUSUAL COMPLEXATION MODEL IN AQUEOUS ACID SOLUTIONS OF NICKEL(II) AND *N,N,N',N',-TETRAKIS*(CARBOXYMETHYL)-*L*-ORNITHINE

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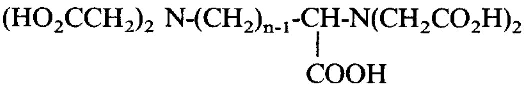
Complex formation for nickel(II) with *N,N,N',N',-tetrakis*(carboxymethyl)-*L*-ornithine (H_5TCO = H_5L) in aqueous solution has been studied by potentiometric, conductometric and spectrophotometric methods. In addition to the complexes (MHL, ML or M_2L_2 and M_2L) previously established for other closely related metal(II): H_5L systems, the formation of Ni_3L_2 in acidic aqueous solution has been established. From 318 potentiometric data for 13 solutions with Ni(II):H_5TCO = 0.5 to 4 and $2 \leq pH \leq 4.6$ (I = 0.1M(KNO_3) and T = 25°C) SUPERQUAD calculations yield the overall formation constants ($\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$) $\log\beta_{111} = 20.82(1)$, $\log\beta_{202} = 36.94(2)$, $\log\beta_{302} = 40.36(5)$ and $\log\beta_{201} = 19.42(12)$. Probable structures for these complexes are discussed.

KEYWORDS: nickel(II), *tetrakis*(carboxymethyl)-*L*-ornithine, stability constants

INTRODUCTION

Four homologous members of the α-carboxypolymethylenediaminotetraacetic acid series (α-cpdt) are known.[1] These acids are obtained by condensation of α, ω-diaminoacids (2,3-diaminopropionic acid, 2,4-diaminobutyric acid, *L*-ornithine and *L*-lysine) with chloro- or bromoacetic acid in an alkaline medium.



$$(HO_2CCH_2)_2\,N\text{-}(CH_2)_{n-1}\text{-}\underset{\displaystyle COOH}{\underset{|}{C}}H\text{-}N(CH_2CO_2H)_2$$

(α-cpdt)

n = 2 H_5CEDT
n = 3 H_5TDB
n = 4 H_5TCO = H_5L
n = 5 H_5TCL

Insertion of the α-carboxy substituent in the 1,n-polymethylenediaminotetraacetic acids (EDTA and its homologues) yields the α-cpdt series of ligands with an unsymmetrical skeleton, having one *N*-substituted iminodiacetic group (IDA) and one *C*-substituted nitrilotriacetic group (NTA) linked by a central $(CH_2)_{n-1}$

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polymethylene chain. As this chain becomes longer the stoichiometry and stability of metal complexes of α-cpdt compounds show the ability of the IDA and NTA groups to cooperate or compete in metal ion chelation.[1] In dilute aqueous solutions (~10^{-3} M) of first-row transition metal(II) ions, the higher members (n = 3 to 5) of the series yield MH_2L, MHL, ML (n = 3) or M_2L_2 (n = 4,5) and M_2L species (as well as $M_2L(OH)$ and/or $M_2L(OH)_2$ hydroxo species). However, the behaviour of the Ni(II):H_5TCO system (but not Ni(II):H_5TCL) deviates from this general pathway. The singular potentiometric, conductometric and spectrophotometric behaviour of Ni(II):H_5TCO solutions strongly suggested the additional formation of Ni_3L_2 in acid media.

We have argued that in more concentrated acid solutions of such metal: ligand systems, neutral MH_3L species could be expected. However, in spite of many attempts to obtain a variety of $MH_3L.nH_2O$ compounds only $CuH_3TDB \cdot 3.5H_2O$ has been obtained; it has been studied by crystallographic and other methods.[1] The main purpose of this work is to carry out a quantitative study of the stoichiometry and stability of Ni(II) complexes with *N,N,N',N',-tetrakis*(carboxymethy)-*L*-ornithine acid (H_5TCO = H_5L) in aqueous solution.

EXPERIMENTAL

Ligand synthesis and reagents

Colourless, polycrystalline samples of *N,N,N',N',-tetrakis*(carboxymethyl)-*L*-ornithine (H_5TCO = H_5L) were obtained by condensation of potassium chloroacetate and *L*-ornithine (Sigma) in an alkaline medium (KOH) at room temperature (two weeks) followed by partial desalination (KCl by-product) of the neutralized solution and the use of an Amberlite IR-120(H) column with water elution. Other details of the procedure (40% yield) are given in ref. 2. All other reagents were of the best available grade (Merck).

Potentiometric and conductometric titrations

All solutions were prepared with CO_2-free, doubly distilled water. Stock solutions of H_5TCO and nickel(II) nitrate were titrated by conventional alkalimetric and complexometric methods,[3] respectively. Starting solutions (100 cm^3) of the ligand and metal: ligand mixtures (0.75/1, 1/1, 1.5/1, 2/1 and 4/1) were prepared with or without background electrolyte (KNO_3, I = 0.1 mol dm^{-3}) for potentiometric or conductometric titrations. All titrations were performed at 25.00±0.05°C by circulating thermostatted water into the appropriate reaction cell and a slow and constant stream of N_2, presaturated through aqueous 0.1 mol dm^{-3} KNO_3, was maintained over the surface of the test solution. Aliquots (25 cm^3) of free ligand and metal-ligand solutions were used to record automatic potentiometric or conductometric titrations on a Radiometer RTS 622 equipped with a Radiometer CDM3 conductometer. The Radiometer potentiometric system (glass and calomel electrodes) was adjusted with standard buffer solutions (pH = 4.00 and 7.02 at 25°C).

For equilibrium constant calculations, aliquots (50 cm^3) of ligand + HCl and metal: ligand mixtures were used to carry out potentiometric measurements on a

Metrohm Dosimat 665 Titroprocesor equipped with a Crison 2002 digital (mV/pH)-meter with combined Ingold electrode (internal reference Ag/AgCl). This potentiometric system was calibrated before and after each experiment by titration of a known amount of HCl (10^{-2} mol dm^{-3}) in KNO_3 (0.1 mol dm^{-3}) against CO_2^- free KOH (0.1 mol dm^{-3}) in KNO_3 (0.1 mol dm^{-3}). For this purpose we have developed the program CALIBRACION on the basis of the calibration procedure proposed by Leporati.[4] For a given calibration titration, we use potential data in the acid range to obtain the concentration of KOH solutions by the Gran method,[5] and then the standard potential of the electrode (E°). The potential data from the alkaline range of the same titration are used to obtain the Kω value and to test the concentration of the KOH titrant reagent. Additional information supplied by CALIBRACION is the slope of electrode response factor (f)*.

Equilibrium constant calculations

Mean values of E°, KOH solution concentration, Kω and f were used in equilibrium constant calculations with the program SUPERQUAD,[6] which was used following IUPAC recommendations.[7,8] The overall protonation constants for the L^{5-} ion of H_5TCO were obtained from 310 potentiometric data of three mixed solutions (H_5TCO + HCl) having 1 to 5×10^{-3} mol dm^{-3} of H_5OTC and $2 \leqslant pH \leqslant 11$. These protonation constants were introduced as fixed values in the refinement of the Ni(II) complex formation constants (log β_{pqr}) defined for

$$p\,Ni + q\,L + r\,H \rightleftharpoons Ni_pL_qH_r$$

as $\beta_{pqr} = [Ni_pL_qH_r]/[Cu]^p[L]^q[H]^r$, where changes are omitted for simplicity. These formation constants were obtained from 318 data from thirteen mixed metal-ligand solutions with ratio Ni(II)/H_5TCO = 0.5 to 4, and $2 < pH < 4.6$, $1.65\times10^{-4} < [Ni(II)] < 2.4\times10^{-3}$ mol dm^{-3} and $1\times10^{-4} < (H_5TCO) < 2\times10^{-3}$ mol dm^{-3}. Values of $\sigma_v = 0.002$ cm^3 and $\sigma_E = 0.1$ mV were used in both protonation and Ni(II) complex formation constant calculations. The restriction of the pH range in these calculations was chosen because of the impossibility of fitting the formation constants of hydroxo species in the alkaline range.

Spectrophotometric study

The electronic spectra (350–870 nm) of Ni(II) nitrate (1 to 2×10^{-3} mol dm^{-3}) and mixed Ni(II):H_5TCO (1/1, 1.5/1 and 2/1) aqueous solutions with different pH values were recorded at 25°C on a Cary 210 Varian spectrophotometer with a 100 mm cell. These solutions were also prepared with $I = 0.1$ mol dm^{-3} (KNO_3). In addition, a series of 25 solutions with $0 < [Ni]/[H_5TCO] \leq 6$, $[H_5TCO] = 1.497\times10^{-3}$ mol dm^{-3} and pH = 4.50 ± 0.05 were used to test the stoichiometric metal:ligand ratio of the studied complexes in weak acid solutions using the molar ratio spectrophotometric method[9,10] with absorbance data at $\lambda = 610$ nm.

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* Ratio of the experimental slope of the electrode response to the slope of the electrode as calculated from the Nernst equation.

RESULTS AND DISCUSSION

Stoichiometry of metal complexes

The potentiometric and conductometric behaviour of the higher members (n = 3 to 5) in the α-cpdt series of H_5L acids[1,2] agrees well with the overall equilibria shown below for

$$H_5L + 3\ OH \rightleftharpoons H_2L + 3\ H_2O$$
$$H_2L + 2\ OH \rightleftharpoons H + 2\ H_2O$$

the addition of *a* (KOH equivs/H_5L mol) = 3 and 5. In the free H_5TCO potentiometric titration (Figure 1) we observe an equivalent point at *a* = 3, whereas a very smooth inflection is recorded at *a* = 4, reflecting the overlap of the two last acid hydrogen titrations.

The potentiometric, conductometric and spectrophotometric results for dilute M(II):H_5L aqueous solutions (M = Mn, Co, Ni, Cu or Zn and H_5L = H_5TDB, H_5TCO or H_5TCL) other than Ni(II):H_5TCO have been explained[1,2] on the basis of the representative behaviour of the solutions with M(II):H_5L = 1/1 and 2/1, according to the formation of MH_2L, MHL, ML (for H_5TDB) or M_2L_2 (with H_5TCO and H_5TCL) and M_2L complexes as well as ML(OH) and $ML(OH)_2$ hydroxo species). Solutions with M(II)/H_5L = 0.5/1 or 4/1 show behaviour expected for 1/1 or 2/1 mixed solutions with 100% of free-ligand or free-metal ion in excess, respectively.[1,2] In general, the equivalent points in potentiometric and/or conductometric titrations are better observed with M = Cu or Ni. For example, potentio metric titrations of

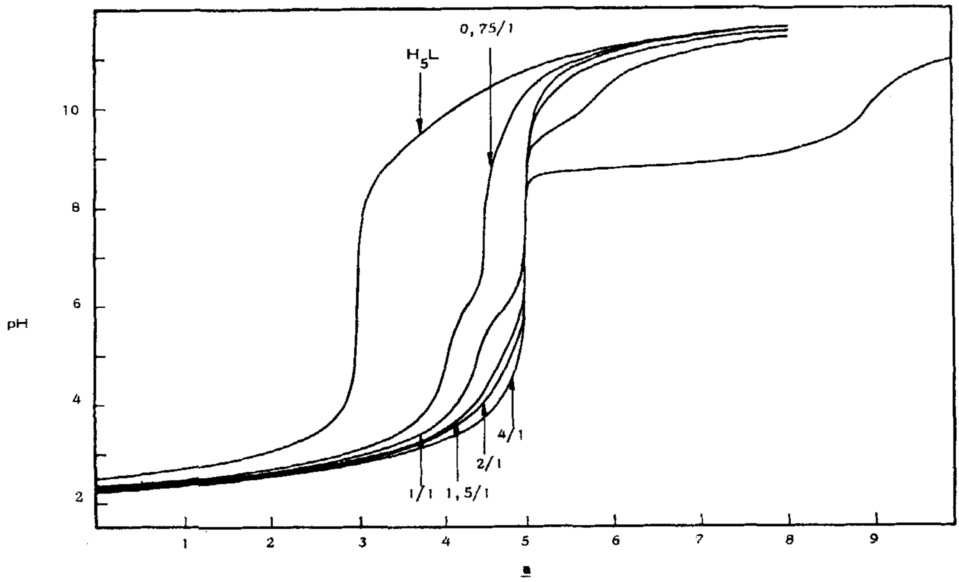


Figure 1 Automatic potentiometric titrations of H_5TCO = H_5L (1.265×10^{-3} mol dm^{-3}) and several Ni(II)/H_5TCO mixed solutions against KOH (0.102 mol dm^{-3}).

equimolar solutions Cu(II)/H_5L = 1/1 (H_5L = H_5TCO^2 and H_5TCL^{11}) show well-defined equivalent points at a = 4 and a = 5, corresponding to the formation of CuHL and Cu_2L_2 (H_5TCO or H_5TCL). The potentiometric behaviour of solutions with Ni(II):H_5TCO = 1/1 with equivalent points at a = 4.33 and a = 5 (Figure 1) deviates from the general behaviour of the other solutions M(II):H_5L = 1/1, including Ni(II):H_5TDB and Ni(II):H_5TCL solutions[11] (with more or less well-defined equivalent points at a = 4 and 5). The singular behaviour of the Ni(II):H_5TCO system (Figure 1) can be rationalized with the assumption that a Ni_3L_2 species could be formed in solutions with Ni(II):$H_5TCO \leq$ e1.5. Accordingly, a representative solution with Ni(II):H_5TCO 1.5/1 shows only a well-defined equivalent point at a = 5, with respect to the following equation.

$$3Ni + 2H_5L + 10OH \overset{a = 5}{\rightleftarrows} Ni_3L_2 + 10H_2O$$

The behaviour of the equimolar mixture Ni(II):H_5TCO = 1/1 is explained by the two equilibria given below.

$$3Ni + 3H_5L + 13OH \overset{a = 13/3 = 4.44}{\rightleftarrows} Ni_3L_2 + H_2L + 13H_2O$$

$$Ni_3L_3 + H_2L + 2OH \overset{a = 4.33 + 2/3 = 5.44}{\rightleftarrows} 3/2Ni_2L_2 + 2H_2O$$

The solution with Ni(II): H_5TCO = 2/1 leads to the overall formation of Ni_2L, whereas the mixture with 0.75/1 ratio (with equivalent points at a = 4, 4.5, 4.75 and 5) or with 4/1 ratio correspond to situations with ligand or metal ion in excess, respectively.

The formation of complexes with metal: ligand ratios 1/1, 3/2 and 2/1 in weak acid solutions (at pH = 4.5) in the Ni(II):H_5TCO system has been confirmed by the means of the method of Yoe and Jones[9,10] (Figure 2). By the same procedure, only complexes with a metal:ligand ratio of 1/1 and 2/1 were found in the Cu(II)/H_5L systems (H_5L = H_5TCO or H_5TCL)[1,2] and Ni(II):H_5TCL^{11} solutions. H_5TCO refined by SUPERQUAD calculations correspond to pK_1 = 1.59, pK_2 = 2.04, pK_3 = 2.63, pK_4 = 9.00 and pK_5 = 10.48±0.01. These data are in reasonable

Equilibrium constants

The protonation constants for the L^{5-} ion of H_5TCO and the overall formation constants of its nickel(II) complexes are given in Table 1. Protonation constants of

Table 1 Protonation and nickel(II) complex formation constants[a] of *N,N,N′,N′,-tetrakis* (carboxymethyl)-*L*-ornithine at 25°C and I = 0.1 mol. dm^{-3} (KNO_3). Standard deviations are given in parentheses.

Protonation of H_5TCO^b	Ni(II) complex formation[c]
$\log\beta_{011}$ = 10.480(1)	$\log\beta_{111}$ = 20.82(1)
$\log\beta_{021}$ = 19.478(1)	$\log\beta_{202}$ = 36.94(2)
$\log\beta_{031}$ = 22.108(1)	$\log\beta_{302}$ = 40.36(5)
$\log\beta_{041}$ = 24.149(8)	$\log\beta_{201}$ = 19.42(12)
$\log\beta_{051}$ = 25.744(2)	logK(NiHL) = 10.34[d]

[a] $pM + qH + rL \rightleftharpoons M_pH_qL_r$, $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$. [b] Number of data: 310, $\sigma = 2.01$, $\chi^2 = 8.98$. [c] Number of data: 318, $\sigma = 3.54$, $\chi^2 = 11.11$. [d] K(NiHL) = [NiHL]/[NI][HL].

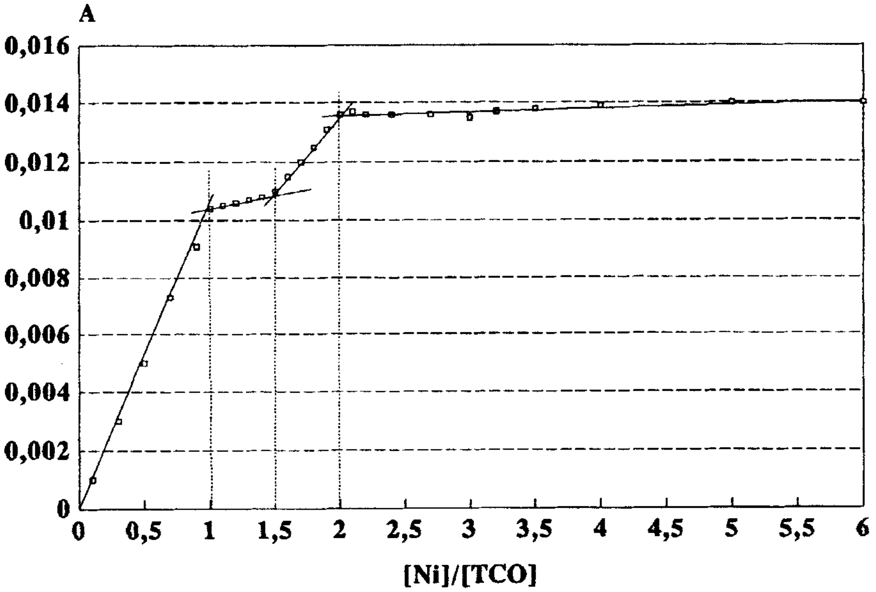


Figure 2 Absorbance at 610 nm of a series of mixed solutions with different Ni(II)/H_5TCO molar ratios (H_5TCO 1.50×10^{-3} mol dm^{-3}) and pH = 4.50±0.01.

agreement with the pK_a values previously obtained from potentiometric data of free-H_5TCO solutions (without addition of a strong acid) by the MINIQUAD program (pK_a = 1.83, 2.29, 2.87, 9.03, 10.45)[1] or by least-squares and algebraic calculations (pK_a = 1.64, 2.46, 2.94, 9.17, 10.54).[2] However, the protonation constants here reported for H_5TCO allow the best stimulation of experimental titrations (Figure 3).

Ni(II) complex formation constants (Table 1) were fitted with the assumption that species $(NiH_xL)_n$, $(Ni_2L_2)_n$, $(Ni_3L_2)_n$ and $(Ni_2L)_n$ could be present in acid solutions. Our results with $\sigma \sim 3$ and $\chi^2 < 12.6$ (which represents a confidence level of 95%)[4] exclude the significant presence of other species with higher protonation degree and/or with $n \neq 1$. By avoiding the influence of hydroxo species (in alkaline or neutral solutions) the $\log\beta_{pqr}$ data allow good simulation of experimental titration curves for representative solutions of the Ni(II):H_5TCO system (pH<4.6). This complex formation model differs from that reported for other closely related systems (M(II):H_5TCO or M(II):H_5TCL)[1,2,11] in the absence of NiH_2L as well as in the formation of Ni_3L_2. The polynuclear nature of this singular complex makes it dependent on the total molar concentration of the ligand H_5TCO as well as the pH and the Ni(II):H_5TCO ratio of the solution. As an example, Ni(II) distribution diagrams (Figure 4) for two representative mixtures with Ni(II):H_5TCO = 1.5/1 show that dilution of the ligand favours dissociation of species with a metal/ligand ratio >1 (Ni_2L and mainly Ni_3L_2) to give species with lower nuclearity and/or lower metal/ligand ratios (1/1 as Ni_2L_2 or NiHL and 1/0 as free Ni(II) aqua-ion).

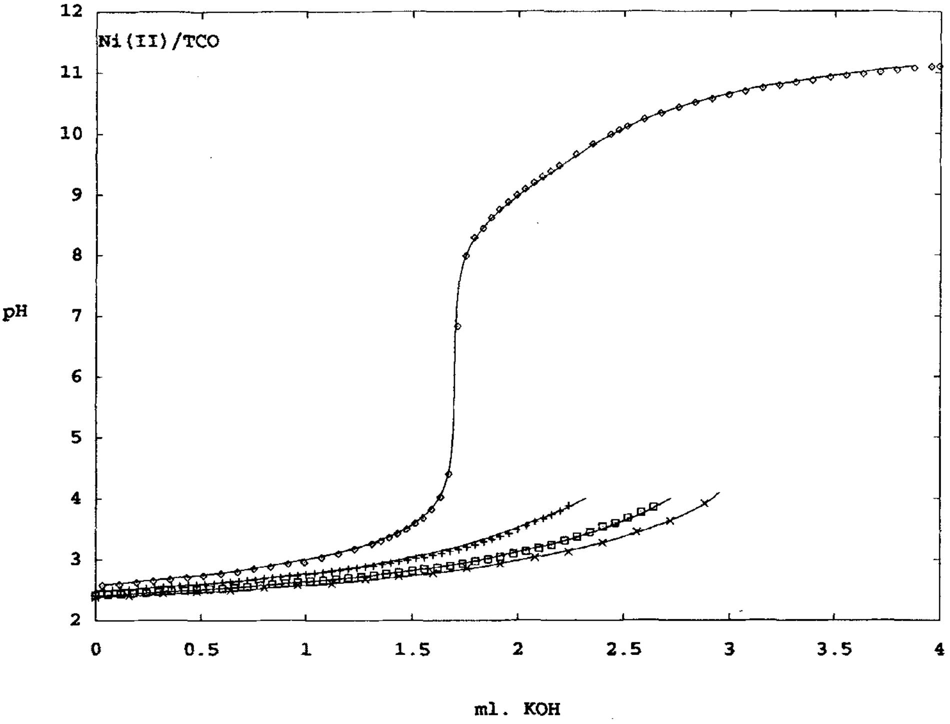


Figure 3 Experimental potentiometric data points and the corresponding simulated titrations (unbroken lines) for free-H_5TCO (1.15×10^{-3} mol dm^{-3}) and mixed solutions Ni(II)/H_5TCO; [H_5TCO] in mol dm^{-3}: 1/1 (1.05×10^{-3}), 1.5/1 (1.19×10^{-3}) and 2/1 (1.25×10^{-3}); [KOH] ~ 0.10 mol dm^{-3}; volume: 50 cm^3.

In order to propose the most probable structure for the studied complexes it is instructive to make stability constant and electronic spectra data comparisons. The electronic spectra of Ni(II) complexes with α-cpdt are typical of octahedral symmetries (more or less distorted).[1] On this basis, the values of λ_{max} and ε_{max}/Ni(II) for the $^1E_g \leftarrow {}^3A_{2g}$ transition band in the studied complexes are given in Table 2.

Table 2 Data for the electronic spectra of solutions in the Ni(II):H_5TCO system.

Ni(II)/H_5TCO	Solution pH	Main species	λ_{max}	ε_{max}/Ni(II)
1/0		$[Ni(H_2O)_6]^{2+}$	660	2.1
1/1	2.35	NiHL	628	5.8(6.9)[a]
1/1	3.60	Ni_3L_2	610	6.8
1/1	6.70	Ni_2L_2	588	8.2(8.1)[a]
1.5/1	2.39	NiHL	622	6.5(6.9)[a]
1.5/1	3.11	Ni_3L_2	606	7.3
1.5/1	7.00	Ni_2L_2	588	8.5(8.1)[a]
2/1	5.53	Ni_2L	618	4.5(5.2)[a]

[a] Data for H_5TCL complexes of the same stoichiometry in ref. 10 are given in parentheses.

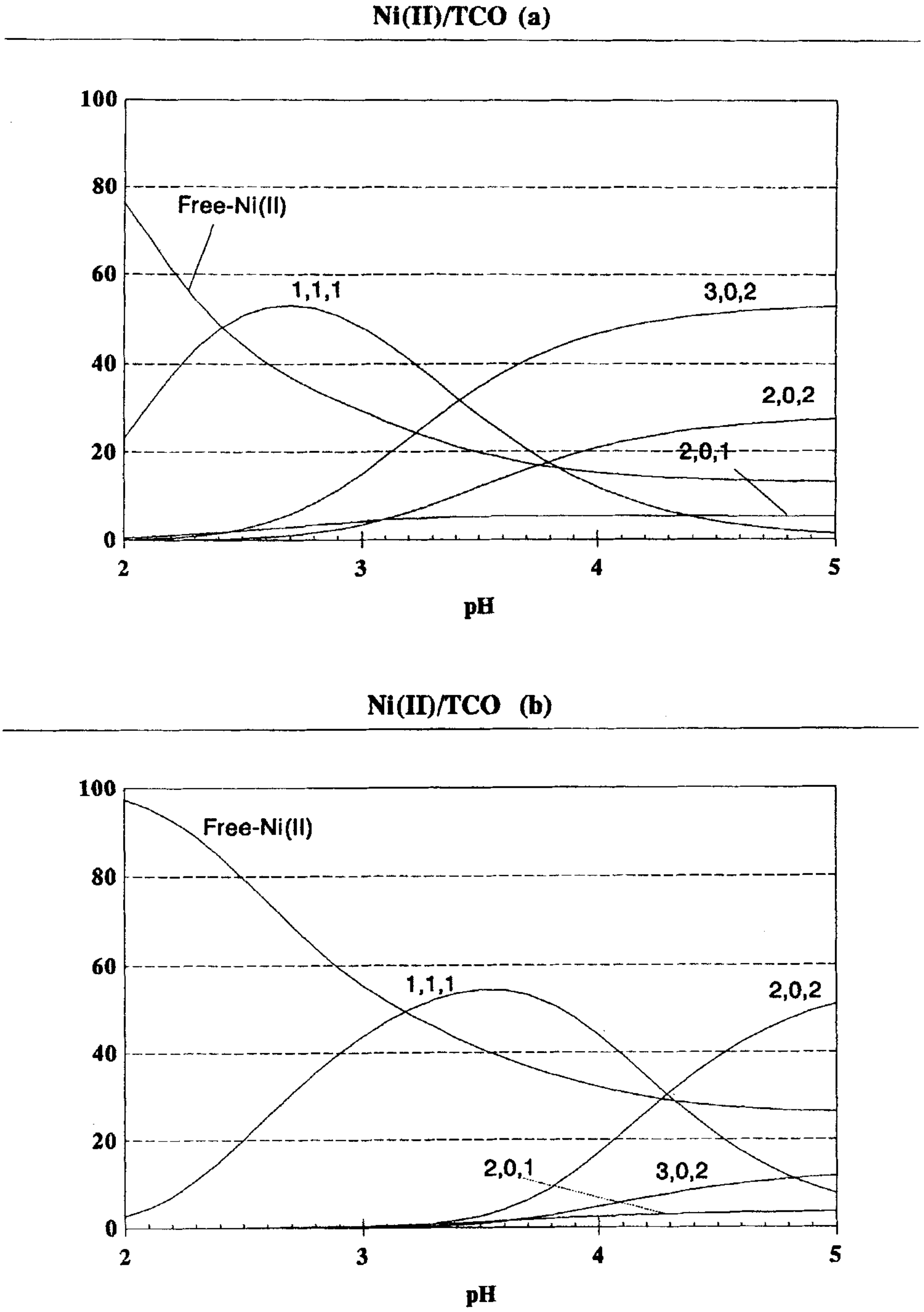
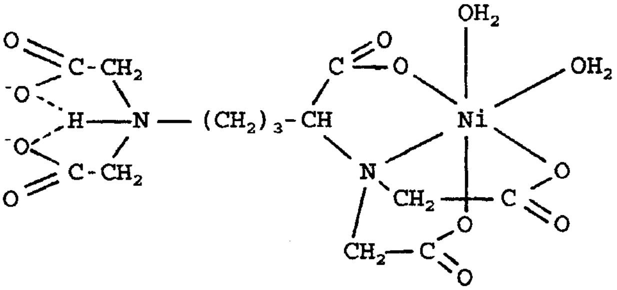
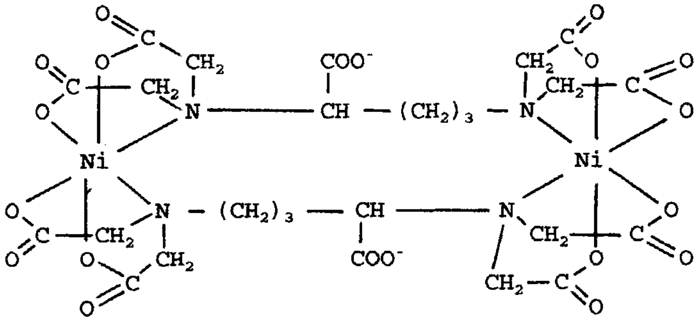


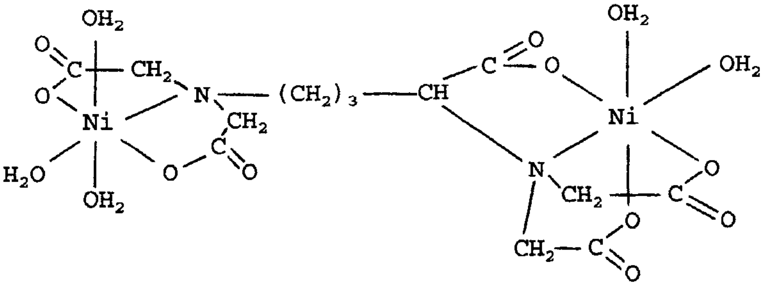
Figure 4 Nickel(II) distribution diagrams in mixed Ni(II)/H_5TCO solutions with 1.5/1 molar ratio: (a) [H_5TCO] = 2.5×10^{-3} mol dm^{-3}; (b) [H_5TCO] = 1.5×10^{-4} mol dm^{-3}.



I (NiHL)



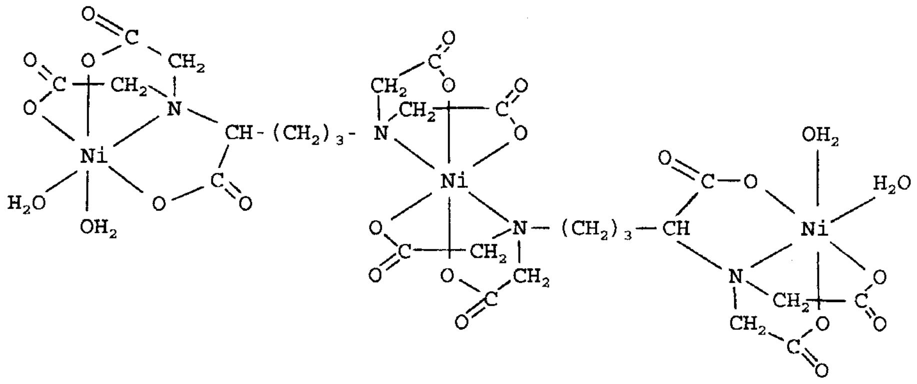
II (Ni_2L_2)



III (Ni_2L)

The complexes NiHL, Ni_2L_2 and Ni_2L of H_5TCO and its homologues H_5TLC have comparable values of ε_{max}/Ni(II) and stabilities (logK(NiHL) = 11.21, logβ(Ni_2L_2) = 31.66 and logβ(Ni_2L) = 19.42 for H_5TCL under the same experimental conditions as in this work.[11] These and other considerations can be rationalized by the structures **I** to **III**. For instance, logK values for NiHL for H_5TCO and H_5TCL (10.34 and 11.21, respectively) are comparable with the literature value of logK for Ni(NTA) (11.26) but higher than logK for Ni(IDA) (8.69).[1] Structure **II** is proposed in accordance with the lack of alkaline hydrolysis of known complexes $(ML)_n$ of H_5TCO and H_5TCL (M = Co, Ni, Cu, Zn).[1,11]

In order to deduce a probable structure for Ni_3L_2 with H_5TCO we keep in mind that both N atoms of the same TCO ligand are unable to chelate the same Ni(II) ion (in a ring of seven atoms), two pentadentate TCO ligands can satisfy only 14 of the 18 coordination positions around three octahedral Ni(II) centres and Ni_3L_2 is resistant to alkaline hydrolysis as compared with Ni_2L (see titration curves in the alkaline range). Indeed, Ni_3L_2 can form Ni_2L_2 and free Ni(II) which undergoes hydrolysis. Furthermore, electronic parameters of Ni_3L_2 (λ_{max} = 608 ± 2 nm, ε_{max} = 6.2 ± 0.4) with an Ni(NTA)-like structure, **I**, and Ni_2L_2(588nm, ε_{max} = 8.4 ± 0.2) with an $[Ni(NTA)(IDA)]_2$-like structure, **II**. On this basis it seems reasonable to propose structure **IV** for Ni_3L_2 with H_5TCO.



IV (Ni_3L_2)

The unusual stability of $Ni_3(TCO)_2$ seems in accordance with the lack of the diprotonated species Ni(H_2TCO) in the complexation model fitted here for the Ni(II):H_5TCO system. One a question remains; why should *N,N,N',N'*-*tetrakis*(carboxymethyl)-*L*-ornithine form the species Ni_3L_2 and the next homologous ligand H_5TCL in the α-cpdt series not? In the literature, there are many examples where a small structural difference between two closely related compounds makes one able and the other unable to exhibit a given property. For example, five or six-membered chelate rings are formed in metal-(1,n-alkyldiamine) complexes whereas homologous seven or larger-membered rings are not expected. The actual reason in the present case is subtle, and remains unclear.

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