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# Copper(II) Complexes with Linear Pentadentate Chelators

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The complexation of $Cu^{2+}$ with 3,6,9-triazaundecane ($Et_2$dien, ded) and its derivatives 4,7,10-triazatridecanedinitrile (nitrile), 4,7,10-triazatridecanedioic acid (acid), 4,7,10-triazatridecanediamide (amide), 1,9-bis(2-hydroxyphenyl)-2,5,8-triazanonane (phenol), and 4,7,10-triazatridecane-1,13-diamine (amine) has been studied by potentiometric and by spectrophotometric pH titrations. With the exception of the tridentate parent substance ded, all these ligands are potentially pentadentate linear chelators with an identical internal 3 N donor set corresponding to dien or ded and two terminal binding groups with strongly differing metal ion affinities. These ligands were considered to be useful for studying a wide range of weak additional interactions in primarily tetracoordinated $Cu^{2+}$ complexes. Also, evidence was obtained for several mono- and diprotonated complexes, where the terminal binding group(s) and in some cases even one nitrogen atom of the dien moiety are detached from the central ion. Spectrophotometry proved to be indispensable not only for structural considerations but also for differentiation between various chemical models, i.e. sets of different complexes. This study demonstrates that spectrophotometric titration is a straightforward method for the investigation of complex equilibrium systems, if appropriate methods for the acquisition and the numerical treatment of the data are applied.

## Introduction

Obviously, the ligating properties of pentadentate linear chelators are somewhat at odds with the basic requirements of the $Cu^{2+}$ ion, which preferably forms tetragonal complexes with four strong interactions in the equatorial plane while one or two additional ligands can be bound much more weakly in the axial positions. There are essentially three solutions to this problem: (i) The fifth binding group of the ligand may be dangling freely in solution. (ii) It may undergo weak apical interaction in a basically still tetragonal complex. (iii) A truly pentacoordinate complex with some distorted-square-pyramidal or trigonal-bipyramidal geometry may be formed.

Some reports on the complexation of strong pentadentate chelators to $Cu^{2+}$ are known, notably with tetren (tetraethylenepentamine, 3,6,9-triazaundecane-1,11-diamine)[1,2] and with several pyridyl-[3] or imidazolyl-[4] containing polyamines. Further ligands of that type may be found among the oligopeptides such as tetraglycine.[5] In this latter case tetracoordinate planar complexes with no appreciable axial interaction are formed at high pH. This is in line with the generally observed reduction in bond order along the $z$ axis, with an increasing number of strong donors such as aliphatic amino or deprotonated amide groups in the equatorial plane.[6] Definitely, more information is needed in order to draw any significant conclusions concerning the importance of a fifth ligating group in linear chelators binding to $Cu^{2+}$. It may be added that a somewhat different situation pertains for macrocyclic ligands with functionalized side arms,[7,8] where pentacoordination is well-known and where a square-pyramidal structure is more or less imposed by the steric requirements of the ligands.

In the present study we report on the complexation of $Cu^{2+}$ by a series of six new ligands **1–6**. All of them can be considered to be derivatives of diethylenetriamine (dien), the $Cu^{2+}$ complexes of which have been studied by several groups.[9-17]

$RCH_2NHCH_2CH_2NHCH_2CH_2NHCH_2R$

**1**, R = $CH_3$ (ded)
**2**, R = $CH_2CN$ (nitrile)
**3**, R = $CH_2CONH_2$ (amide)
**4**, R = $CH_2COOH$ (acid)
**5**, R = $CH_2CH_2NH_2$ (amine)
**6**, R = 2-$C_6H_4OH$ (phenol)

The numbering of the ligands follows the increasing coordination power of the substituents. Only the position of **3** is ambiguous because complexes with the neutral or with the much stronger deprotonated amide group are both possible. With the exception of the tridentate ded **1** these ligands are in principle capable of forming pentacoordinate complexes with two terminal six-membered rings fused to two internal five-membered rings of the dien moiety.

The following questions were the main subject of this study: (1) Do ligands **2–6** indeed behave as pentadentate chelators in interactions with $Cu^{2+}$? (2) If so, can we arrive at some conclusions concerning their structure by studying their electronic absorption spectra? (3) With L = dien the following complexes have been found in previous studies:[14,15,17] $CuL^{2+}$, $CuLH_{-1}^{+}$, $CuL_2H^{3+}$, $CuL_2^{2+}$. In one report even the formation of $CuLH^{3+}$ has been claimed.[16] Are the corresponding species also observed with the ligands **1–6**?

Both potentiometric and spectrophotometric titrations have been used to tackle the above questions. Potentiometry still is the standard method for the determination of stability constants, while spectrophotometry has the advantage of yielding additional information through the spectral characteristics of the species. Also, spectrophotometry is superior to pH measurements in strongly acidic or basic solutions where the buffering capacity of $H_3O^+$ or $OH^-$ obscures any complexation equilibria. Some difficulties related to the use of spectrophotometric data in the determination of equilibrium constants[18] have been successfully overcome in this laboratory. (i) The necessary large body of high-quality spectra is obtained

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by a fully automatic titration setup, giving routinely raw data with an overall standard error of 0.0002–0.0003 absorbance unit.[19] (ii) Representation of the original spectra in their eigenvector space greatly reduces the amount of data to be handled in the nonlinear least-squares treatment.[17] (iii) The problem of iterative refinement of a large number of unknowns has been overcome by eliminating the molar absorptivities of the unknown species through the algorithm incorporated into our program ELORMA.[20] In a recent comparative study potentiometric and spectrophotometric titrations thus yielded results of essentially equal reproducibility, but the spectrophotometric method was significantly superior in the discriminatory power with respect to different models of complexation.[21]

## Experimental Section

**Syntheses. 3,6,9-Triazaundecane Trihydrobromide (ded).** The tritosylate of ded was obtained by adding 10 mL (122 mmol) of ethyl iodide to a solution of 13.5 g (28.7 mmol) of the disodium salt of tritosylated dien[22] in 200 mL of dimethylformamide and stirring for 1 h at 85 °C. The product crystallized after the addition of ethanol; mp 122–23 °C. Anal. Calcd for $C_{29}H_{39}N_3O_6S_3$: C, 56.02; H, 6.32; N, 6.76; S, 15.47. Found: C, 55.98; H, 6.42; N, 6.69; S, 15.31.

The tosyl groups were removed by treatment with HBr/acetic acid/phenol for 3 h at 60 °C. The trihydrobromide precipitated after cooling and addition of 500 mL of diethyl ether and was recrystallized from methanol/water/HBr: mp 250–52 °C; overall yield for 2 steps 40%. Anal. Calcd for $C_8H_{24}Br_3N_3$: C, 23.90; H, 6.02; N, 10.45. Found: C, 23.87; H, 6.11; N, 10.30. $^1$H NMR ($D_2O$): $\delta$ 1.32 (t, 6 H, $CH_3$), 3.21 (q, 4 H, $CH_2CH_3$), 3.53 (s, 8 H, $CH_2CH_2NH$).

**4,7,10-Triazatridecanedinitrile Trihydrochloride (Nitrile).** Acrylonitrile (188 g, 3.55 mol) was slowly added to 180 g (1.76 mol) of dien, and the mixture was stirred for 20 h at 20 °C. A 100-g portion of the crude product was purified as the trihydrochloride by recrystallization from methanol/water/HCl: mp 219–22 °C; yield 65 g (42%). Anal. Calcd for $C_{10}H_{22}Cl_3N_5$: C, 37.69; H, 6.96; N, 21.98. Found: C, 37.6; H, 7.0; N, 21.7. $^1$H NMR ($D_2O$): $\delta$ 3.0–3.7 (m, unresolved).

**4,7,10-Triazatridecanediamide Trihydrochloride (Amide).** The nitrile (2.00 g, 6.28 mmol) was hydrolyzed in 20 mL of concentrated HCl for 20 min at 40 °C. After evaporation, the residue was purified from acidic impurities by passing it through an anion-exchange column in the $OH^-$ form. The ligand was recrystallized from methanol/water/HCl: mp 221–22 °C; yield 50%. Anal. Calcd for $C_{10}H_{26}Cl_3N_5O_2$: C, 33.86; H, 7.39; Cl, 29.98; N, 19.74. Found: C, 33.91; H, 7.16; Cl, 30.01; N, 20.00. $^1$H NMR ($D_2O$): $\delta$ 2.73 (t, 4 H, $CH_2CONH_2$), 3.35 (t, 4 H, $CH_2CH_2CONH_2$), 3.45 (s, 8 H, $CH_2CH_2NH$).

**4,7,10-Triazatridecanedioic Acid Sulfate Hydrogen Sulfate (Acid).** The nitrile (10.0 g, 31.3 mmol) was hydrolyzed for 6 h in 55 mL of 5 M boiling $H_2SO_4$. The sulfate hydrogen sulfate was recrystallized from acetone/water/$H_2SO_4$: mp 214–16 °C, yield 7 g (50%). Anal. Calcd for $C_{10}H_{25}N_3O_{12}S_2$: C, 27.09; H, 5.68; N, 9.48; S, 14.46. Found: C, 27.0; H, 5.6; N, 9.6; S, 14.3. $^1$H NMR ($D_2O$): $\delta$ 2.88 (t, 4 H, $CH_2COOH$), 3.42 (t, 4 H, $CH_2CH_2COOH$), 3.53 (s, 8 H, $CH_2CH_2NH$).

**4,7,10-Triazatridecane-1,13-diamine Pentahydrobromide (Amine).** A solution of 55.4 g (206 mmol) of *N*-(bromopropyl)phthalimide in 180 g of dimethylformamide was added to a solution of 63 g (103 mmol) of the disodium salt of tritosylated dien[22] in 600 g of dimethylformamide and stirred for 6 h at 100 °C. The fully protected amine crystallized by addition of ethanol; mp 159–60 °C. Anal. Calcd for $C_{47}H_{49}N_5O_{10}S_3$: C, 60.05; H, 5.25; N, 7.45; S, 10.23. Found: C, 60.1; H, 5.0; N, 7.5; S, 10.2.

The phthalimide groups were removed by boiling an ethanolic solution of 20 g of protected amine with 4 mL of hydrazine hydrate for 3 h. An 8.5-g portion of the crude product was detosylated in a mixture of 90 mL of HBr/acetic acid and 10 g of phenol for 3 h at 60 °C. The pentahydrobromide crystallized after addition of 500 mL of diethyl ether and was recrystallized from methanol/water/HBr: mp 266–68 °C; overall yield 40%. Anal. Calcd for $C_{10}H_{32}Br_5N_5$: C, 19.31; H, 5.19; N, 11.26. Found: C, 19.33; H, 5.05; N, 11.00. $^1$H NMR ($D_2O$): $\delta$ 2.17 (m, 4 H, $CH_2CH_2CH_2$), 3.28 (m, 8 H, $NHCH_2CH_2CH_2NH_2$), 3.65 (s, 8 H, $CH_2CH_2NH$).

**1,9-Bis(2-hydroxyphenyl)-2,5,8-triazanonane Trihydrochloride (Phenol).** Salicylaldehyde (21.0 g, 0.172 mol) was added slowly to 8.6 g (83.5 mmol) dien and stirred for 1 h to form the Schiff base, which was dried under vacuum and hydrogenated in methanolic solution with 2 g of a 10 % Pd/C catalyst under normal pressure and temperature. The ligand was recrystallized as the trihydrochloride from ethanol/water/HCl: mp 207–08 °C; yield 70%. Anal. Calcd for $C_{18}H_{28}Cl_3N_3O_2$: C, 50.83; H, 6.64; Cl, 25.04; N, 9.89. Found: C, 50.73; H, 6.81; Cl, 25.01; N, 9.80. $^1$H NMR ($D_2O$): $\delta$ 3.58 (s, 8 H, $CH_2CH_2NH$), 4.35 (s, 4 H, $CH_2$-aryl); 7.18 (m, 8 H, aryl).

The purity of each ligand was further checked by pH titration (vide infra). The molecular weights thus determined agreed to 0.5% or better with the theoretical values.

**Materials.** NaOH and HCl (both Titrisol), KCl, and $CuSO_4 \cdot 5H_2O$ (all of p.A. grade), were from Merck AG, Darmstadt, FRG, and were used without further purification. Twice-distilled water was used throughout. pH buffers (pH 4.00 and 7.00) were from Metrohm AG, Herisau, Switzerland.

**Instrumentation.** Potentiometric titrations were obtained with a microprocessor-controlled Metrohm E 600 digital pH meter as described recently.[23] Spectrophotometric titrations were done on a Cary 118 C spectrophotometer with a fully automatic setup[19,24] under control of an Apple II desk computer. Infrared spectra were taken on a Beckman IR 420.

**Data Reduction.** Data reduction was done on a Hewlett-Packard HP 9835 desk computer with 128K memory, equipped by a HP 72225A plotter and a Heathkit H14 printer. Data were transferred from the potentiometric[23] and the spectrophotometric[19] data acquisition systems to the HP 9835 through a HP 98036A serial interface.

Equilibrium constants were calculated from potentiometric data with the program TITFIT.[25] Spectrophotometric data were first represented in their eigenvector basis.[17] This leads to a significant reduction of the amount of data to be handled in the iterative refinement of the equilibrium constants, without any loss of significant information. The program used was a modification of ELORMA[20] with automatic generation of optimal subroutines and using analytical derivatives according to the ideas developed for TITFIT.[25] The program[26] only needs estimates for the equilibrium constants while the molar absorptivities are eliminated from the iterative refinement and are obtained noniteratively from the final set of equilibrium constants by linear regression.

**Measurements.** Spectrophotometric and potentiometric experiments were done at 25.0 °C in aqueous solution of constant ionic strength ($I$ = 0.5 M, (KCl)) under nitrogen and were repeated once. The potentiometric titrations were done with two ligand concentrations in the presence of 0, 0.40, and 0.90 equiv of $Cu^{2+}$, respectively. NaOH (0.40 M) was used to titrate 25 or 100 mL of solutions, which were 2.40 or 0.600 mM (amide, amine, phenol), 4.00 or 1.00 mM (nitrile, ded), or 2.00 and 0.50 mM (acid) in the ligand concentration, respectively.

After calibration of the potentiometer to 0.001 log unit using buffers of pH 4 and 7, a standard mixture of HCl and $CH_3COOH$ was titrated each day before starting the actual experiments. The instrument was recalibrated whenever the protonation constant of $CH_3COOH$ differed by more than 0.01 log unit from our standard value of log $K^H_{CH_3COOH}$ = 4.60 and/or the activity coefficient of $H^+$ (0.85) or the ion product of water ($pK_w$ = 13.88) indicated incorrect electrode response.

In the spectrophotometric experiments, 30 increments of 0.01 mL of NaOH ($I$ = 0.500 M (KCl)) were added to 2.30 mL of complex solution. The ligand concentrations were chosen such that optimum changes in absorbance were obtained, i.e. 3.20 and 6.40 mM for ded, 4.00 and 8.00 mM for the nitrile, 1.90 and 4.80 mM for the amide, 4.00 and 20.0 mM for the acid, and 1.60 and 3.20 mM for the phenol and for the amine. Each solution was titrated in the presence of 50.0 and 90.0% $Cu^{2+}$. When it later became apparent that some com-

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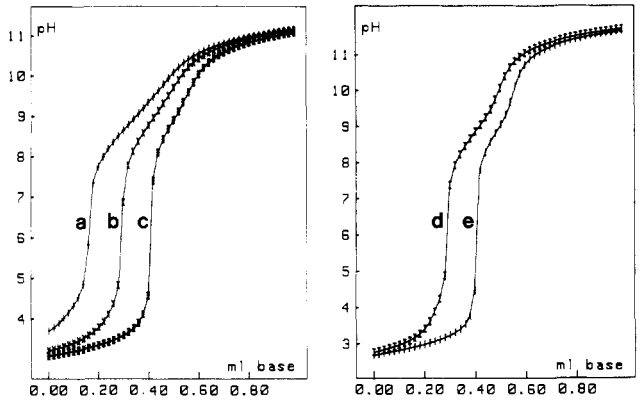


**Figure 1.** Potentiometric titration curves of the amide (—, calculated curves): (a) 0.6 mM ligand, no $Cu^{2+}$; (b) 0.6 mM ligand, 0.5 equiv of $Cu^{2+}$; (c) 0.6 mM ligand, 0.9 equiv of $Cu^{2+}$; (d) 2.4 mM ligand, 0.5 equiv of $Cu^{2+}$; (e) 2.4 mM ligand, 0.9 equiv of $Cu^{2+}$.

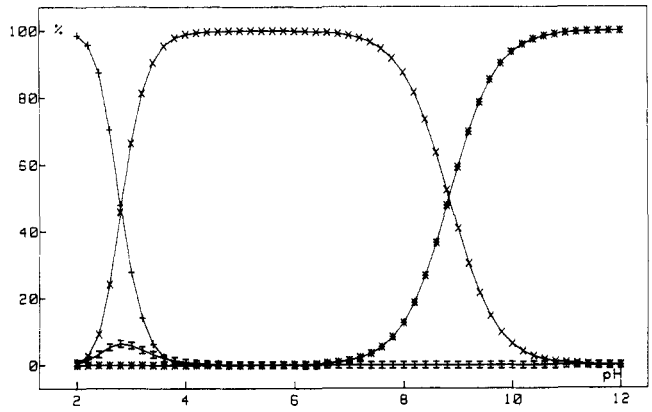


**Figure 2.** Species distribution curves for the amide (2.4 mM ligand, 0.9 equiv of $Cu^{2+}$): (+) $Cu_{aq}^{2+}$; (I) $CuLH^{3+}$; (×) $CuL^{2+}$; (*) $CuLH_{-1}^{+}$.

plexation takes place at very low pH, additional mixtures of 5.00 mM ligand, 4.00 mM $Cu^{2+}$, and 10.0 mM HCl were titrated three times for each system. The absorption of every solution was measured between 800 and 550 nm at 10-nm intervals and was stored on a floppy disk together with the pH.

IR spectra were measured of 0.15 M deuterated complex solutions in $D_2O$. Irtran cells and Parafilm-coated NaCl windows of 0.025 mm path length were used below and above pD 10, respectively.

## Results and Discussion

Ligand protonation constants and stability constants of the $Cu^{2+}$ complexes are compiled in Tables I and II, respectively.

Weighted means, log $\bar{K}$, and their standard errors, $\sigma_{\log K}$, are given. Standard errors were calculated according to eq 1 (absolute weights) and 2 (relative weights), and the larger results are indicated in the tables.

$$\sigma_{\log K}^2 = \frac{1}{\sum_i 1/\sigma_{i,\log K}^2} \quad (1)$$

$$\sigma_{\log K}^2 = \frac{\sum_i (\log K_i - \log \bar{K})^2/\sigma_{i,\log K}^2}{\sum_i (N-1)/\sigma_{i,\log K}^2} \quad (2)$$

Standard errors $\sigma_{i,\log K}^2$ from the individual titration curves were used as the weighting factors. Mixed constants, using $10^{-pH}$ instead of $[H^+]$, are given throughout. Transformation into concentration constants can be done with a proton activity coefficient of 0.85, as has been determined from the control titrations (vide supra). In the absence of systematic errors, reasonable confidence limits would be given by three times the standard error of the stability constants. While this is true for most cases, a few of the stability constants show somewhat

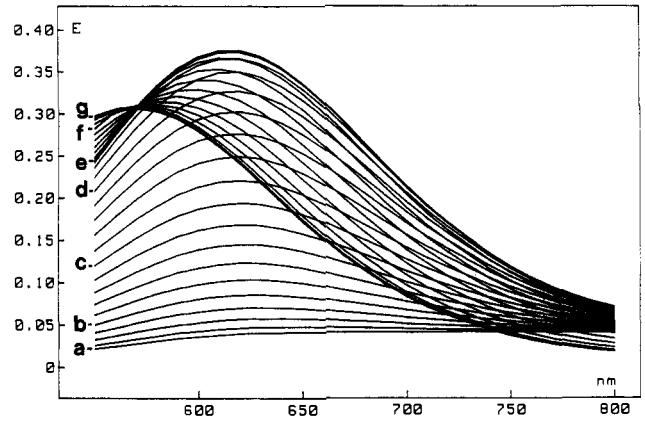


**Figure 3.** Spectrophotometric titration of the amide (5 mM ligand, 4 mM $Cu^{2+}$, 10 mM HCl). pH: (a) 2.16; (b) 2.35; (c) 2.61; (d) 2.98; (e) 5.25; (f) 9.08; (g) 10.86.

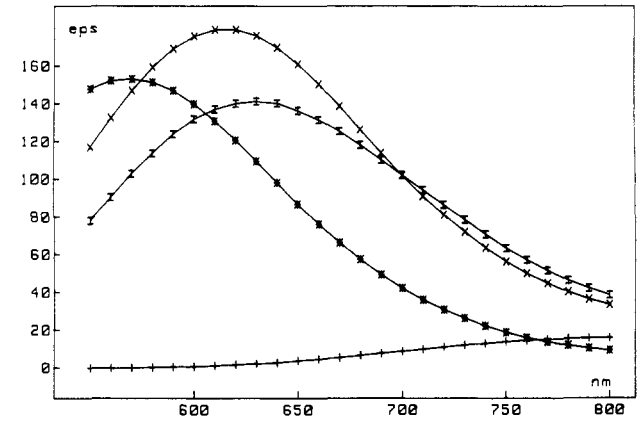


**Figure 4.** Calculated spectra of the amide: (+) $Cu_{aq}^{2+}$; (I) $CuLH^{3+}$; (×) $CuL^{2+}$; (*) $CuLH_{-1}^{+}$.

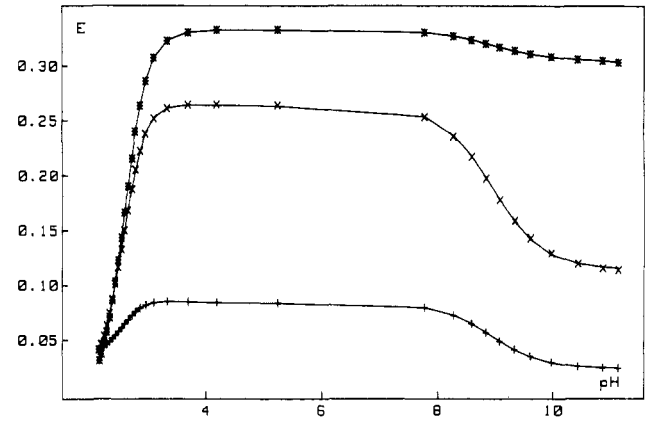


**Figure 5.** Spectrophotometric titration curves with the amide (5 mM ligand, 4 mM $Cu^{2+}$, 10 mM HCl). Experimental points (—, calculated curves): (*) 580 nm; (×) 680 nm; (+) 780 nm.

larger differences between potentiometric and spectrophotometric results. Likely this is due to the fact that several species are formed at low pH where the potentiometric method is notoriously inaccurate since the ligands behave almost like strong acids in the presence of metal ions. We are therefore inclined to prefer the spectrophotometric results, but more evidence is needed to substantiate this assumption.

Absorption maxima and molar absorptivities of all complexes are compiled in Table III together with their standard errors. The absorption maxima were obtained from the calculated molar absorptivities of three points around the maximum using quadratic interpolation. The results from different titrations agreed within 1–2 nm for all well-defined species

Table I. Ligand Protonation Constants[a] and Their Standard Errors

| ligand | $\log K^{H}_{LH}$ | $\log K^{H}_{LH_2}$ | $\log K^{H}_{LH_3}$ | $\log K^{H}_{LH_4}$ | $\log K^{H}_{LH_5}$ |
|---|---|---|---|---|---|
| dien[b] | 10.18 | 9.41 | 4.83 | | |
| ded | 10.51 (0.01)[c] | 9.85 (0.01) | 4.31 (0.01) | | |
| nitrile | 8.86 (0.01) | 5.83 (0.01) | 3.65 (0.01) | | |
| amide | 9.34 (0.01) | 8.31 (0.01) | 3.93 (0.01) | | |
| acid | 9.99 (0.01) | 9.31 (0.01) | 4.40 (0.01) | 3.55 (0.01) | 2.97 (0.01) |
| amine | 10.72 (0.03) | 10.10 (0.02) | 8.94 (0.01) | 7.89 (0.03) | 3.96 (0.03) |
| phenol | 11.06 (0.01) | 10.41 (0.01) | 9.09 (0.01) | 7.94 (0.02) | 4.18 (0.04) |

[a] $K^{H}_{LH_x} = [LH_x]/([LH_{x-1}][H^+])$, proton activity, $10^{-pH}$, used for $[H^+]$. [b] See ref 40. [c] Calculated standard errors of less than 0.01 log unit were not considered to be realistic because of systematic instrumental uncertainties.

Table II. Stability Constants[a] (with Standard Errors) of $Cu^{2+}$ Complexes Obtained from Spectrophotometric and Potentiometric Titrations[b]

| ligand | $\log K^{H}_{CuLH_2}$ | $\log K^{H}_{CuLH}$ | $\log K^{Cu}_{CuL}$ | $\log K^{H}_{CuL}$ |
|---|---|---|---|---|
| dien | | 3.25[c] | 16.55[d] | 9.49[d] |
| ded (s) | *e* | 3.68 (0.05) | 15.05 (0.03) | 9.56 (0.03) |
| (p) | | 3.46 (0.07) | 15.01 (0.01) | 9.46 (0.01) |
| nitrile (s) | *e* | 2.30 (0.17) | 13.00 (0.05) | 9.44 (0.04) |
| (p) | | 1.69 (0.13)[f] | 12.79 (0.01) | 9.28 (0.01) |
| amide (s) | *e* | 2.31 (0.05) | 16.28 (0.04) | 8.98 (0.02) |
| (p) | | 1.86 (0.07)[f] | 16.10 (0.01) | 8.83 (0.01) |
| acid (s) | 2.37 (0.04) | 3.73 (0.01) | 18.47 (0.04) | |
| (p) | 2.79 (0.02) | 3.72 (0.01) | 18.36 (0.01) | |
| amine (s) | 3.27 (0.02) | 8.97 (0.02) | 22.11 (0.09) | |
| (p) | 3.31 (0.03) | 8.99 (0.01) | 21.65 (0.05) | |
| phenol (s) | 3.99 (0.01) | 8.65 (0.01) | 22.60 (0.04) | |
| (p) | 4.08 (0.01) | 8.49 (0.01) | 22.53 (0.02) | |

[a] $K^{H}_{CuLH_x} = [CuLH_x]/([CuLH_{x-1}][H^+])$, proton activity, $10^{-pH}$, used for $[H^+]$; $K^{Cu}_{CuL} = [CuL]/([Cu][L])$. [b] s, results from spectrophotometry; p, results from potentiometry. [c] From ref 16. [d] From ref 40. [e] Species not observed. [f] Species not significant according to *F* test for potentiometric titrations but established through results from spectrophotometry.

(maximum concentration above 50%).

In Figures 1–6, a selection of the experimental data and of the results of the numerical treatment is shown for the amide.

In Figure 1 we have the experimental points of one set of potentiometric titrations, together with the calculated titration curves (solid lines). Figure 2 gives the species distribution pertaining to the titration curve with high (2.4 mM) ligand concentration and 0.9 equiv of copper. Obviously, the species $CuLH^{3+}$ (I) is formed at low pH, and its maximum concentration is less than 10%. Both facts are detrimental to the determination of this species by potentiometry. Indeed, according to the error analysis, its formation is not statistically significant as far as the potentiometric data are concerned.

Figure 3 gives the 31 original spectra obtained from one spectrophotometric titration. An isosbestic point, which is somewhat broadened by the effects of dilution, is observed at high pH.

Figure 4 shows the spectra of the individual species $Cu^{2+}$ (+), $CuLH^{3+}$ (I), $CuL^{2+}$ (×), and $CuLH_{-1}^{+}$ (*). Obviously, not only $Cu^{2+}$, $CuL^{2+}$, and $CuL_{-1}^{+}$ are found but also $CuLH^{3+}$, which has a well-defined and reasonable spectrum (cf. Table III).

Figure 5 gives the titration curves (absorbance vs. pH) for the same experiment at 580 (*), 680 (×), and 780 (+) nm. The fit is essentially perfect, the overall standard error for this particular titration being only 0.00075 absorbance unit (all wavelengths included). In Figure 6, finally, the effect of reducing the chemical model to $Cu^{2+}$, $CuL^{2+}$, and $CuLH_{-1}^{+}$, is shown. Quite in line with the result obtained by subjecting the data to the *F* test ($F = 20$, highly significant), Figure 6 clearly suggests that $CuLH^{3+}$ has to be included in order to achieve an acceptable fit. With the complete model, the residuals are generally less than twice the overall standard errors

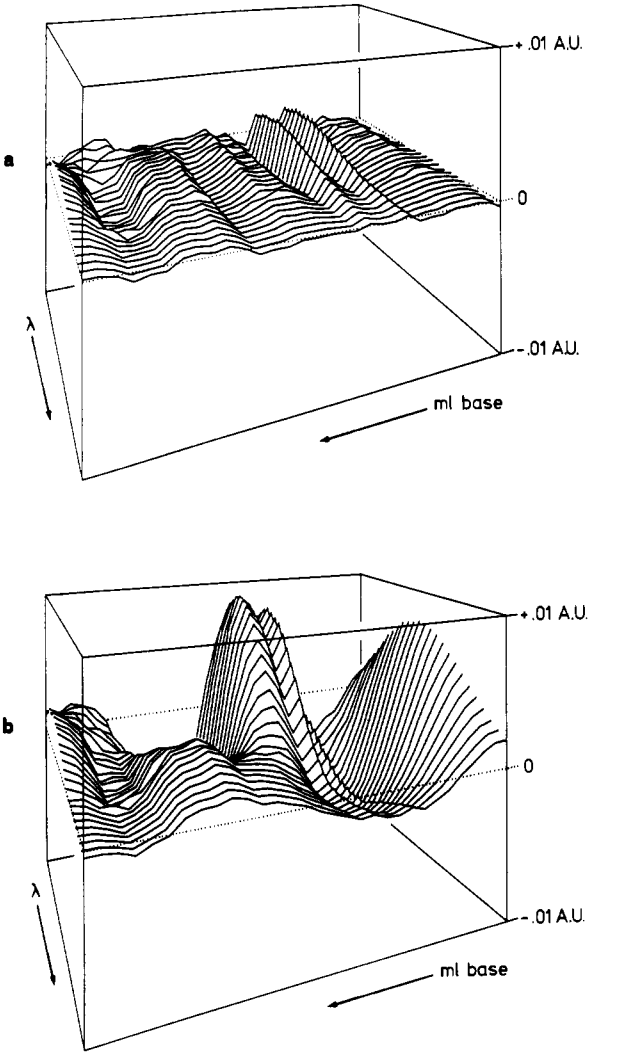


**Figure 6.** Three-dimensional plot of residuals (absorbance units, A.U.) from spectrophotometric titrations (conditions as in Figure 3): (a) complete model, including $Cu^{2+}$, $CuLH^{3+}$, $CuL^{2+}$, and $CuLH_{-1}^{+}$; overall standard error 0.00075 absorbance unit; (b) same, without $CuLH^{3+}$; standard error 0.0034 absorbance unit.

and do not show any conspicuous peaks. On the other hand, the reduced model is obviously off, with the most prominent deviations at low and medium pH, where $CuLH^{3+}$ is formed and then deprotonated to $CuL^{2+}$. Thus, spectrophotometry is very well suited to distinguish between the two models, and $CuLH^{3+}$ is a necessary species. As already mentioned, $CuLH^{3+}$ has previously been postulated by one research group[16] for the unsubstituted dien but has not been found in a series of other studies of this system.[9-15,17] $CuLH^{3+}$ has not been found, either, in a detailed study of a series of alkyl-substituted diethylenetriamines[27] (no spectrophotometric ti-

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Table III. Absorption Maxima and Molar Absorptivities of the $Cu^{2+}$ Complexes

| ligand | $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CuLH_2$ | | CuLH | | CuL | | $CuLH_{-1}$ | |
| dien[a] | | | | | 615 | 82 | 605 | 73 |
| ded | | | 645 (11) | 126 (24) | 631 (2) | 158 (7) | 614 (3) | 120 (6) |
| nitrile | | | 653 (16) | 145 (55) | 644 (2) | 169 (2) | 603 (2) | 114 (1) |
| amide | | | 632 (5) | 137 (15) | 615 (1) | 176 (5) | 569 (1) | 150 (4) |
| acid | 641 (16) | 121 (30) | 615 (1) | 172 (7) | 629 (1) | 171 (7) | | |
| amine | 631 (7) | 146 (17) | 573 (1) | 187 (8) | 585 (1) | 214 (10) | | |
| phenol | 633 (2) | 155 (8) | 595 (1) | 202 (4) | 680 (2) | 160 (3) | | |

[a] From ref 40.

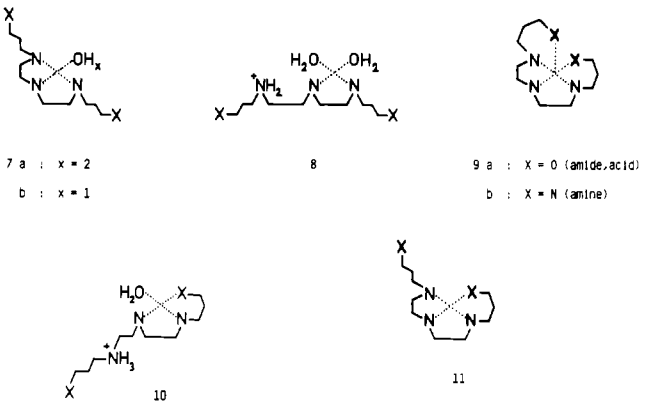
trations were included in that case). Ring opening of chelates with nitrogen donors in the equatorial plane is, however, well-known for complexes with condensed chelate rings having a 5,6-ring sequence[28] and for tetraaza polyamines such as trien[29-32] and related compounds.[33] Results such as those given in Figure 6 and also statistical analysis using the *F* test do not leave any reasonable doubt about the existence of $CuLH^{3+}$ with our ligand.

**Discussion of the Individual Ligands. ded.** The ligand protonation constants of ded are not very different from those of dien although L and $LH^+$ are by about 0.4 log unit more basic for ded, while the opposite is true for $LH_2^{2+}$. Also, the stabilities of $CuL^{2+}$ (**7a**) and $CuLH_{-1}^+$ (**7b**) are similar to those of the corresponding complexes with dien, but some slight steric hindrance may be reflected through the decreased stability of $CuL^{2+}$ by 1.5 orders of magnitude. A protonated species $CuLH^{3+}$ (**8**) is formed around pH 3.5, in line with the corresponding results as found by one research group for dien.[16] Contrary to the results for dien, the well-characterized 1:2 complexes $CuL_2H^{3+}$ and $CuL_2^{2+}$ have not been observed with ded.

Of course, ded cannot possibly be more than tridentate, and the species $CuLH^{3+}$, $CuL^{2+}$, and $CuLH_{-1}^+$ do not give any gross structural problems. However, the molar absorptivity of $CuL^{2+}$ is increased over that of $Cu(dien)^{2+}$ by a factor of 2, and also the absorption maximum is shifted to longer wavelengths by 16 nm. Further, a relatively small red shift of only 14 nm is observed upon protonation to $CuLH^{3+}$. All these observations cannot be explained on the basis of the donor groups and their ligand field increments[34,35] alone and indicate some distortion from a tetragonal structure in $CuL^{2+}$.

**Nitrile.** The inductive effect of the nitrile group reduces the basicity of this ligand relative to ded by more than 6 log units for three protons. The reduction of the $CuL^{2+}$ stability relative to that of $Cu(ded)^{2+}$ is much less significant, about 2 orders of magnitude. This does not automatically imply coordination of the nitrile group since similar effects of electron-withdrawing groups have been known since the early days of polyamine complexation studies.[36] Otherwise, the nitrile behaves like ded. The two ligands need the same set of species $CuLH^{3+}$, $CuL^{2+}$, and $CuLH_{-1}^+$, and deprotonation of $CuL^{2+}$ occurs at similar pH values. No evidence for binding of the nitrile group to $Cu^{2+}$ is obtained by IR, since the vibrational band stays at 2250 $cm^{-1}$ for both the free and the complexed ligand. On the other hand, the drastic blue shift from 644 nm for $CuL^{2+}$ to 603 nm for $CuLH_{-1}^+$ is clear evidence for structural reorganization upon deprotonation. Pentacoordination with or without weak interaction of $Cu^{2+}$ and the nitrile groups thus may be invoked for $CuL^{2+}$.

**Chart I**




It should be noted that potentiometric and spectrophotometric data do not very well correlate in the case of the nitrile. No convincing explanation can be given presently; some error may be introduced by partial hydrolysis of the ligand, which would more strongly affect the spectrophotometric data collected over a period of about 2 h rather than 30 min in the case of potentiometric titrations (Chart I).

**Amide.** The overall basicity of this ligand is reduced by 3 orders of magnitude relative to ded, but the complex stability is increased by a factor of 10. The complexing properties of the neutral amide group are well-known. For tetradentate ligands such as 3,7-diazanonanediamide a stabilization of roughly 3 orders of magnitude per amide group participating in a five-membered chelate ring has been estimated.[37] A comparison of the complex formation and ligand protonation constants of $NH_3$ ($\log K_{ML}^M - \log K_{HL}^H = 4.24-9.32 = -5.08$)[38] and of glycinamide ($\log K_{ML}^M - \log K_{HL}^H = 5.40 - 8.05 = -2.65$)[39] leads to the same conclusion.

With the present ligand, six- rather than five-membered terminal chelate rings are formed and the amount of stabilization is expected to be less pronounced. This is indeed the case, but a quantitative statement cannot be made, since inductive effects (vide supra, nitrile) and stabilization by chelation are difficult to separate and the question of the relative effects of the first and the second amide group is even more tricky to tackle.

Coordination of the neutral amide group is obvious not only from the stability constants but also from the IR spectra. The free ligand has its principal amide stretching frequency at 1623

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$cm^{-1}$. Upon protonation of the amino groups, this is shifted to 1635 $cm^{-1}$. For the complex $CuL^{2+}$ we would expect some intermediate value, if the amide group was not involved in coordination to $Cu^{2+}$. In fact, two bands, at 1605 and 1620 $cm^{-1}$, are observed, however. The former is ascribed to the more strongly coordinated amide in the equatorial plane, **9**, the latter to a much weaker apical interaction, as has been postulated for the ternary $Cu^{2+}$/dien/L-alaninamide[40] complex. The spectrophotometric results are in line with this interpretation. With the amide, the absorbance maximum of $CuL^{2+}$ at 615 nm is at a considerably shorter wavelength than with ded and the nitrile and can only be explained by the formation of an additional chelate ring. Also, the $\lambda_{max}$ of 632 nm for $CuLH^{3+}$ would seem to be too small, if the ligand were only coordinated through two nitrogen atoms. That a neutral O-coordinated amide group may lead to a significant blue shift relative to other oxygen donors is exemplified by the complex $CuL^{2+}$ with 3,7-diazanonanediamide.[37] The $\lambda_{max}$ of 628 nm is extremely small for a complex having the $N_2O_2$ donor set and can only be explained by coordination of both terminal amide groups[35] in the equatorial plane of the tetragonal complex.

Although deprotonation of $CuL^{2+}$ to $CuLH_{-1}^{+}$ again occurs around pH 9 in the case of the amide, the origin of the additional proton is different: the amide group is ionized and consequently bound through the deprotonated nitrogen. This can be implied not only by comparison with related ligands but also by the concomitant strong blue shift to 569 nm and most definitely by the corresponding new IR band at 1535 rather than at 1605 $cm^{-1}$. Deprotonation of the second amide group has not been observed up to pH 12, in line with the previously observed reluctance of $Cu^{2+}$ to form complexes with a deprotonated amide group in apical position.[40] In 3 M NaOD, the second amide band disappears slowly, giving rise to a single stretching frequency at 1540 $cm^{-1}$. The visible spectrum does not change appreciably in the same period, and the absorption maximum remains at 570 nm. These two observations indicate a slow hydrolysis of the neutral amide group, while the strongly coordinating deprotonated amide function remains unaltered.

**Acid, Amine, and Phenol.** The acid, the amine, and the phenol not only are obvious pentadentate chelators but also are capable of binding up to five protons. Therefore, analogous compositions of the complexes may have structural implications that are different from those for the ligands discussed so far. The set of $Cu^{2+}$ complexes is identical for these three ligands, viz. $CuLH_2$, CuLH, and CuL (charges omitted, those of the amine complexes are by two units more positive than those with the acid or the phenol). No hydroxo species was observed with any of these ligands.

The logarithms of the cumulative protonation constants (sum of log $K^{H}_{LH_n}$ values in Table I) are 30.2, 41.6, and 42.9 for the acid, the amine, and the phenol, respectively. The stability constants of CuL increase in the same order: log $K^{Cu}_{CuL}$ = 18.4, 21.9, and 22.6 (cf. Table II).

In $CuLH_2$, all three ligands probably act as tridentate chelators, but the mode of binding remains ambiguous. The symmetric structure **7a** corresponding to $Cu(ded)^{2+}$ or $Cu(dien)^{2+}$ would involve only five-membered chelate rings and may be preferred on that basis. However, an asymmetric complex **10** with only one dangling arm is also possible and in line with the observed opening of one chelate ring of the dien moiety for ligands **1–3** or dien itself.[16] Unfortunately, all ligating groups of the amine and of the phenol have roughly equal affinity to $Cu^{2+}$, and discrimination between **7a** and **10** is not possible on a theoretical basis. Carboxylates, on the other hand, are less strongly binding to $Cu^{2+}$ than are amino groups, but they are present in free form at low pH, while the amino functions are strongly protonated around pH 3, where $CuLH_2$ and CuLH are formed. The equilibrium constants log $K^{H}_{CuLH_2}$ = 2.6 and log $K^{H}_{CuLH}$ = 3.7 are rather close to the corresponding protonation constants of the two carboxylate groups in the free ligand: log $K^{H}_{LH_5}$ = 3.0 and log $K^{H}_{LH_4}$ = 3.5. However, chelate rings with amino[16,29-32,41] or carboxylate[42] donors are apparently opened at roughly equal pH values, and distinction between **7a** and **10** is again not possible on the basis of theoretical arguments. The d–d* absorption spectra are not of much help in this context either. For the amine and the phenol, all donor groups are rather close in the spectrochemical series and no distinction is possible on this basis; for the acid, the spectrum itself is not known well enough.

For CuLH we can safely assume a quasi-planar structure **11** with one dangling arm for all three ligands. Absorbance maxima are all shifted to shorter wavelengths by 15 to 60 nm relative to the 3 N coordinated species $Cu(ded)^{2+}$, indicating additional coordination in the equatorial plane. Some distortion from an ideal square-planar complex is indicated by the relatively high molar absorptivities (170–200 $M^{-1}$ $cm^{-1}$, cf. Table III), but very strong distortion would not be in line with the positions of the absorbance maxima.

The question of the coordination of the fifth binding group in CuL can be answered in the affirmative for all ligands. In each case a red shift of the absorption maximum is observed. If deprotonation of the dangling arm in **11** were not accompanied by coordination, then a very small blue shift through inductive effects would be expected. The size of the red shift is dramatically different for the acid and the amine on the one side and the phenol on the other side. For the first two ligands the red shift is only about 14 nm, and this is explained by some weak additional apical interaction in an essentially still tetragonal complex (**9**). It should be noted that coordination of the fifth binding group could not have been concluded safely from the potentiometric data alone: log $K^{H}_{CuLH}$ is 3.72 and 8.99 for the acid and the amine, respectively. On the basis of the corresponding ligand protonation constants, deprotonation of the terminal binding groups would be expected around these pH values even without coordination. Thus, apical interaction, while definitely established through the spectrophotometric results, is only weak and will not contribute significantly to the stability of the complexes. The situation is quite different with the phenol as ligand. Here, the red shift observed upon deprotonation of CuLH amounts to almost 100 nm. Interaction of the fifth binding group is accompanied by a substantial reorganization of the complex. We assume that this species is genuinely pentacoordinate and that all five ligand atoms are bound with roughly equal strength to $Cu^{2+}$. It presently remains unclear whether it corresponds more closely to a square-pyramidal or to a trigonal-bipyramidal structure.

**Discriminatory Power of Potentiometric and of Spectrophotometric Titrations.** As can be seen from Table II, spectrophotometric and potentiometric data generally yield roughly equal standard errors for the individual equilibrium constants. However, spectrophotometric titrations are significantly superior to potentiometric data with respect to differentiation between several models of complexation.[21] This is especially prominent for complexes formed at low or at very high pH. In fact, in the present study the formation of $CuLH^{3+}$ with the nitrile and the amide and of $CuLH_2$ with the acid could not have been deduced on the basis of the potentiometric data alone. In all cases, the reduction of the overall variance upon introduction of these acidic species was not significant ac-

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cording to the *F* test, and calculated titration curves with and without the additional species were just barely discernible. For several individual titration curves the calculation even failed to converge to physically sound, i.e. positive, values for all stability constants with the complete model.

Quite to the contrary, the results from the spectrophotometric titrations were always highly significant according to the *F* test. As shown in Figure 6 for one of the experiments with the amide, visual inspection also very clearly suggests the necessity of the complete model. These conclusions are even further substantiated by the reasonable spectra that are calculated for these minor species. Thus, while in no way advocating the abolition of potentiometric titrations, we are strongly in favor of also including the spectrophotometric variety whenever this is feasible. It is to be expected that the latter method will prove to be essential for establishing the correct chemical model in many cases.

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# Solution Studies of Systems with Polynuclear Complex Formation. 5. Copper(II) and Cadmium(II) D-(+)-Tartrate Systems

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The complex formation in aqueous solution between copper(II) or cadmium(II), respectively, and D-(+)-tartrate has been studied in the pH range of 4–11 in 0.5 mol $L^{-1}$ $KNO_3$ at 25 °C. The emphasis is on the alkaline region with the ligand in excess and on the formation of polynuclear, especially binuclear, complex species. A potentiometric method using glass and metal ion selective electrodes has been applied. The experimental data indicate the formation of mononuclear, binuclear, and more highly polymerized species. The evaluated stability constants are presented in Table I. The stabilities of the proton complexes of the ligand have been evaluated in the same ionic medium. The existence of heteronuclear copper–cadmium D-tartrate complexes has been probed spectrophotometrically by the lack of pairwise electronic excitations in the UV region.

## Introduction

Metal tartrate complexes in solution exhibit manifold possibilities in composition and structure. The ligand contains two carboxyl and two hydroxyl groups, and the complexing agent may be expected to form chelate rings including one metal ion as well as bridges between several metal ions.[1,2]

We have an interest in polynuclear complex formation in hydroxy carboxylate systems, with a main emphasis on citrate systems.[3-5] The degree of polynuclearity of metal chelates seems to be governed mainly by the ligand as exemplified by the dimeric species of formulas $M_2H_{-1}L^0$, $M_2H_{-1}L_2^{3-}$, and $M_2H_{-2}L_2^{4-}$ formed in the copper(II) and cadmium(II) citrate systems ($H_3L$ = citric acid).[3,4]

Crystal structure investigations of various basic metal tartrates show discrete dimeric units in the solid state.[1,2] It seems reasonble to assume that the same type of dimeric units also will appear in solution.

The existence of dimeric species in copper(II), lead(II), and antimony(III) tartrate solutions was first suggested by Kahlenberg[6] in 1895 from freezing point depression and emf data, but these findings were opposed by later investigations.[7] In 1957, Lefebvre[8] made a reinvestigation of the cupric tartrate system by means of combined pH and pCu (=−log $[Cu^{2+}]$) measurements and found evidence for an octanuclear complex, $Cu_8H_{-10}T_6^{6-}$, ($H_2T$ = tartaric acid) in neutral solutions, whereas in alkaline solutions there is an equilibrium, $Cu_3H_{-6}T_3^{6-} + 3T^{2-} \rightleftarrows 3CuH_{-2}T_2^{4-}$, which is dependent on the excess of ligand. The existence of the complexes $Cu_8H_{-10}T_6^{6-}$ and $CuH_{-2}T_2^{4-}$ was confirmed in a later investigation.[9]

The copper(II) tartrate complexes in acid and neutral solutions have been thoroughly investigated by Bottari et al.[10,11] and by Johansson.[12-14] According to the potentiometric studies, mononuclear and binuclear complexes are formed in weakly acidic solutions. In the copper(II) D-tartrate system the dimer $Cu_2T_2^0$ undergoes a stepwise ionization reaction to form $Cu_2H_{-1}T_2^-$ and $Cu_2H_{-2}T_2^{2-}$ (p*K* values are 4.40 and 4.56) when the pH value of the solution is increased to neutrality.[13] At the same time, an additional condensation takes place, yielding an octanuclear complex, $Cu_8H_{-10}T_6^{6-}$.

Studies of complex formation in the cadmium(II)–tartrate system are scarce.[15,16] In an investigation of the alkaline pH range, the ionization of the $CdT^0$ complex to $CdH_{-1}T^-$ and $CdH_{-2}T^{2-}$ was determined (p*K* values are 8.59 and 10.28 at 33 °C). It was assumed that the complexes formed are mononuclear.

The aim of the present paper was to investigate the metal chelates formed with triply as well as quadruply ionized tartrate. The investigation was carried out for two different

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