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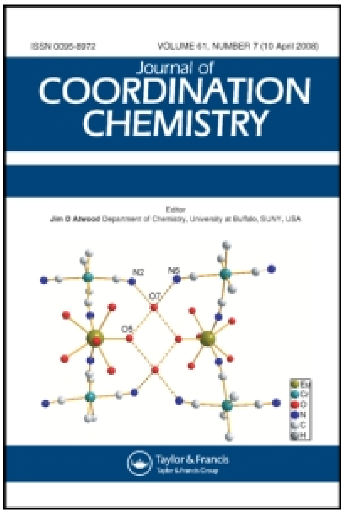

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Complexation of [S,S,S]- and [R,S,R]-isomers of *N-bis*[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II) and Zn(II) ions in aqueous solution

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In a search for environmentally friendly metal chelating ligands for industrial applications, the protonation and complex formation equilibria of [S,S,S]- and [R,S,R]-isomers of *N-bis*[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCA6) with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II) and Zn(II) ions in aqueous 0.1 M NaCl solution were studied at 25°C by potentiometric titration. The model for complexation and the stability constants of the different complexes were determined for each metal ion using the computer program SUPERQUAD. With all metal ions (M^{n+}), stable ML^{n-6} complexes dominated complex formation for both isomers. Differences in complexation models were found for binuclear species.

Keywords: Chelating agent; Stability constants; *N-bis*[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid; [S,S,S]-isomer; [R,S,R]-isomer

1. Introduction

The ability of aminopolycarboxylates such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) to form stable metal complexes has been widely utilized in analytical chemistry and industry. Both these ligands are excellent chelating agents for a variety of large-scale industrial applications. However, the persistence of EDTA and DTPA and their metal complexes in nature may cause environmental harm. During the past few years, the nonbiodegradability of these ligands and their consequent accumulation in the environment has been the cause of a great deal of concern. [1–6] Both are virtually nonbiodegradable in waste water treatment plant conditions [7–9] and they are difficult to remove from bleaching effluents and may be capable of remobilizing toxic heavy metal ions from sediments [10, 11]. EDTA is on the EU priority list of substances for risk assessment.

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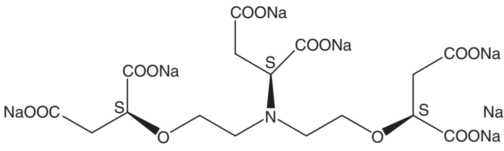
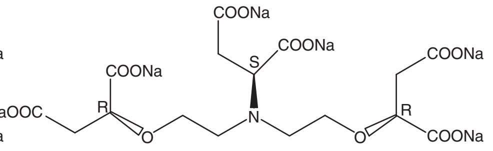
In accordance with the conclusions of the EU Risk Assessment Report [12] there is a need for limiting the risks which EDTA continues to pose to the environment. This conclusion is reached because of the high levels of EDTA released into the environment due to its use in industrial detergents, by paper mills, by circuit board producers and during recovery of EDTA-containing wastes. Characterisation of these release scenarios show that they pose risks to aquatic organisms [12]. Replacement of EDTA and DTPA by more environmentally friendly chelating agents wherever possible would be highly desirable.

Alternative chelating agents with complex forming properties comparable to those of EDTA and DTPA and showing better biodegradability, but having lower nitrogen content, have been tested in both pulp bleaching [13–17] and detergent [18] applications as well as complexation studies [17–22]. Pulp usually contains traces of transition metal ions, such as iron and manganese, which catalyze the decomposition of hydrogen peroxide, peracids and other oxygen-based chemicals during bleaching [23] resulting in excess chemical consumption and reduced pulp strength. Thus, removal of transition metal ions from the pulp by chelation is an essential step when bleaching is done with oxygen-based chemicals. Both EDTA and DTPA are commonly used in such chelation steps. Ethylenedisuccinic acid (EDDS), iminodisuccinic acid (ISA) and N-bis[2-(1,2-dicarboxyethoxy)ethyl] aspartic acid (BCA6) are suitable as biodegradable alternatives in some bleaching applications for removal of transition metal ions from pulp. [13–17]

For EDDS the biodegradability depends significantly on the isomeric form of the compound: the [S,S]-isomer is completely biodegradable while the [R,R]-isomer is only marginally degraded, e.g. in the standard Sturm test [24]. In bleaching application tests, BCA6 has proven to be an excellent choice [17] and its biodegradability [25–29] as well as its complex formation as an isomeric mixture with several metal ions [17, 21, 22] has been studied previously. BCA6 have the advantage that its Mn-complexes are inert in peracetic acid solution, in contrast to Mn-EDTA and Mn-DTPA complexes, which are capable of decomposing peroxy compounds catalytically. EDDS and ISA do not have this advantage. Thus, BCA6 can be partly circulated back into different stages of the bleaching process, which is not possible when using EDTA, DTPA, EDDS or ISA. Therefore, use of BCA6 gives an environmental advantage by reducing the amounts of bleaching chemicals, fresh water and the number of process stages necessary in bleaching. [30] Although possible differences in the biodegradability of BCA6-isomers are not known, an interest in studying the complexation of isomers of BCA6 arose from the significant difference in biodegradability of EDDS-isomers. In this study, the complexation of [S,S,S]- and [R,S,R]-isomers of BCA6 with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II) and Zn(II) ions is reported.



[S,S,S]-BCA6



[R,S,R]-BCA6

2. Experimental

2.1. *Preparation of BCA6 and stock solutions of metal ions*

The ligand isomers were produced by Kemira as sodium salts using stereo centers from L- and D-malic and aspartic acid as reported previously [31]. The purity of the preparations was confirmed using NMR and potentiometric titration. Aqueous Cu(II), Mn(II), Mg(II), Zn(II) and Ca(II) chloride solutions were prepared by dissolving $CuCl_2$, $MnCl_2$ and $MgCl_2$ hydrates in distilled water and ZnO and CaO in aqueous hydrochloric acid. Fe(III) chloride solution was prepared from a Fixanal ampoule (Riedel-de Haën). The metal contents of the stock solutions were standardized by EDTA titration. The acid content of the metal solutions were determined by titration with 0.1 M NaOH solution after liberation of the H^+ ions by cation exchange.

2.2. *Potentiometric measurements*

Protonation and complex formation equilibria were studied in aqueous 0.1 M NaCl at 25.0°C through a series of potentiometric EMF titrations carried out with a Schott-Geräte GmbH titrator TPC2000 and utilizing titration software TR600 version 5.00. The cell arrangement for the measurement of the hydrogen ion concentration, $[H^+]$ was as follows:

$$-\mathrm{RE}|\ \text{equilibrium solution}|\ \mathrm{GE}+ \tag{1}$$

where GE denotes a glass electrode, Schott N2680, and RE is Hg, Hg_2Cl_2 | | 0.1 M NaCl.

Expression (2) is valid assuming the activity coefficients to be constant.

$$E = E_0 + 59.157 \log[\mathrm{H}^+] + j_{\mathrm{H}}[\mathrm{H}^+] + j_{\mathrm{OH}}[\mathrm{OH}^-] \tag{2}$$

The cell parameter E_0 and the liquid junction coefficient j_H, valid in acidic solutions, were determined for each titration by addition of a known amount of HCl to the background electrolyte. The value of the liquid junction coefficient j_{OH}, valid in basic solutions, was determined periodically. Only stable emf readings (0.2 mV/2–3 min) were used in the calculations.

During measurements of the metal complex equilibria, aqueous 0.1 M NaOH or 0.1 M HCl was added to the solution. The ratio of the total concentrations of metal, C_M, to ligand, C_L, was held constant. The initial concentrations were varied within the limits $0.0004\,\mathrm{M} \le C_M \le 0.0021\,\mathrm{M}$ and $0.0006\,\mathrm{M} \le C_L \le 0.0021\,\mathrm{M}$, covering metal-to-ligand ratios from 3 : 1 to 1 : 2. Three to six independent titrations were carried out for each system. The number of data points used in the calculation of the stability constants varied from 168 to 467 in the pH ranges 2.5–11.2 for Mg(II), 2.6–11.0 for Ca(II), 2.6–11.0 for Mn(II), 1.9–8.8 for Fe(III), 2.0–10.8 for Cu(II) and 2.2–11.1 for Zn(II). In some titrations, the upper pH values were limited by the appearance of a precipitate or very slow attainment of equilibrium. The reproducibility and reversibility of the equilibria were tested by performing forward (increasing pH) and backward (decreasing pH) titrations.

2.3. *Data treatment*

Protonation/deprotonation of the ligands was controlled by addition of HCl/NaOH. Curves of Z_H *versus* pH were drawn to visualize the experimental data sets. Z_H describes the average number of H^+ ions added or liberated per mole of ligand and is given by the relation

$$Z_H = \frac{(C_H - [H^+] + k_w[H^+]^{-1})}{C_L} \tag{3}$$

where C_H denotes the total concentration of protons calculated over the zero level HL^{5-}, H_2O and M^{n+}.

In evaluating the equilibrium constants, the following two-component equilibria were considered:

$$HL^{5-} \rightleftharpoons L^{6-} + pH^+, p = 1;\ \beta_{-p01} \tag{4}$$

$$pH^+ + HL^{5-} \rightleftharpoons H_{p+1}L^{p-5}, p = 1 - 6;\ \beta_{p01} \tag{5}$$

Metal complex formation can be characterized by the general three-component equilibrium

$$pH^+ + qM^{n+} + \mathrm{r}(HL^{5-}) \rightleftharpoons (H^+)p(M^{n+})q(HL^{5-})r;\ \beta_{pqr} \tag{6}$$

The hydrolysis of metal ions can be written

$$pH^+ + qM^{n+} \rightleftharpoons (H^+)p(M^{n+})q;\ \beta_{pq0} \tag{7}$$

The protonation constants of the ligands and the hydrolysis constants of the metal ions [32] were considered as known parameters in the evaluation of the three-component system (6).

Mathematical analysis of the systems involves a search for complex models (*pqr*-triplets) and equilibrium constants for the complexes that best describe the experimental data. The calculations were carried out with SUPERQUAD. [33] The sample standard deviation s and the χ^2-statistics used as criteria in selection of the complex models were those given by the program.

3. Results and discussion

3.1. *Protolytic properties of [S,S,S]- and [R,S,R]-isomers of BCA6*

The neutralization titrations show that stepwise deprotonation of H_7L^+ to HL^{5-} occurs in the pH range from acidic to neutral (Z_H from 6 to 0). HL^{5-} is the major species from pH 6 to pH 8.5 when $Z_H = 0$. The negative Z_H values reached in the pH-range from neutral to 10 show that in alkaline solution one proton (from the amino nitrogen, HL^{5-} to L^{6-}) can leave the ligands (figures 1 and 2). The equilibrium constants for reactions (4) and (5) obtained in the final refinements are listed in table 1 and the results are compared with the protonation of the BCA6-mixture [17]. For comparison with EDTA and DTPA [34], the protonation of BCA6 is also rewritten in the form given in table 2.

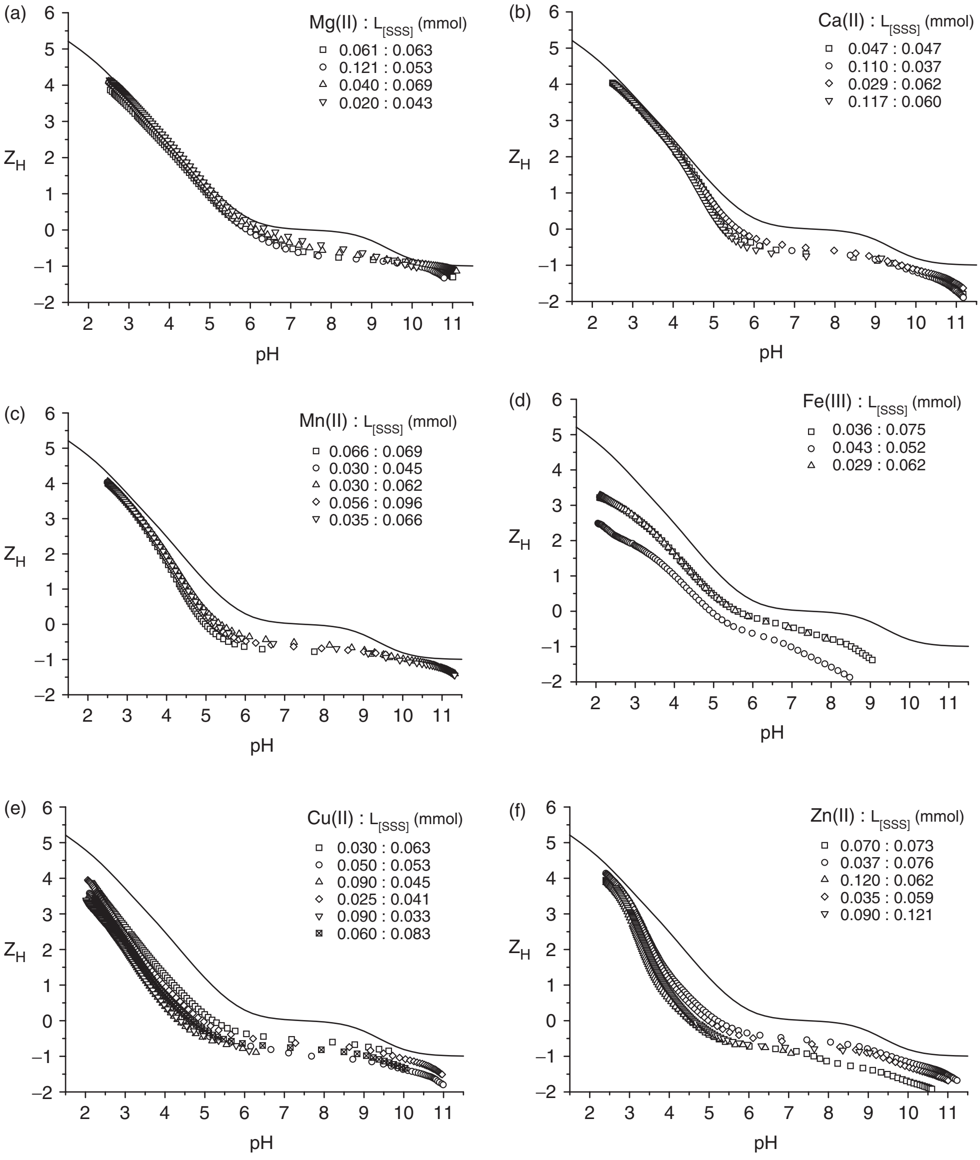


Figure 1. Z_H *vs.* pH for complexation of (a) Mg(II), (b) Ca(II), (c) Mn(II), (d) Fe(III), (e) Cu(II) and (f) Zn(II) with [S,S,S]-BCA6 (Z_H *vs.* pH for [S,S,S]-BCA6 = solid line).

3.2. *Complexation with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II) and Zn(II)*

Analysis of the data was initiated by drawing curves of Z_H *versus* pH (figures 1 and 2). In all systems, Z_H reaches a value of −1 with increasing pH, indicating the coordination of BCA6 to metal in the form of L^{6-}. ML^{n-6} is the predominant species formed in all systems. Z_H values lower than −1 were obtained for all metal ions, indicating the presence of hydroxo complex species, $M(OH)L^{n-7}$. Formation of the acidic species MHL^{n-5}, MH_2L^{n-4} and MH_3L^{n-3} was also found for all metal ions and formation of

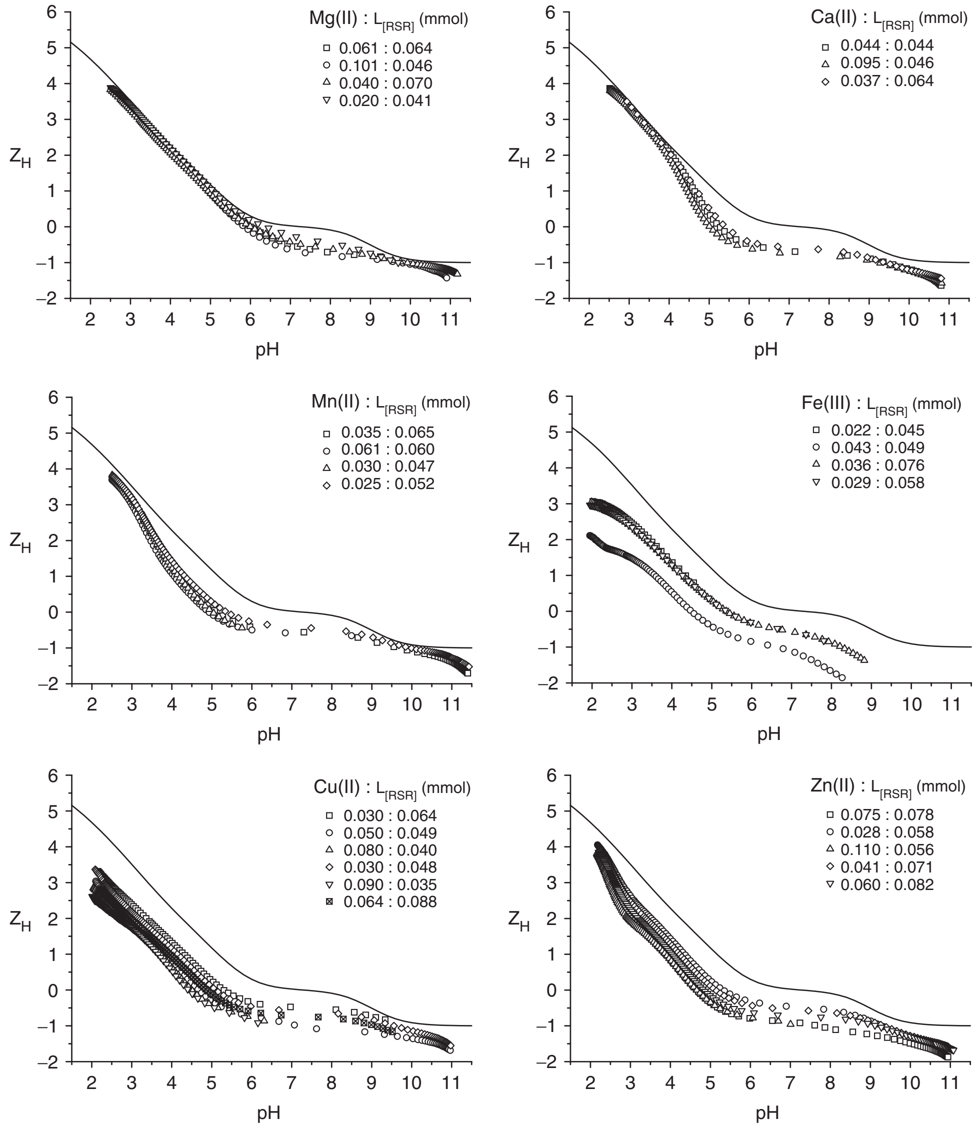


Figure 2. Z_H *vs.* pH for complexation of (a) Mg(II), (b) Ca(II), (c) Mn(II), (d) Fe(III), (e) Cu(II) and (f) Zn(II) with [R,S,R]-BCA6 (Z_H *vs.* pH for [R,S,R]-BCA6 = solid line).

MH_4L was seen for all metal ions except Fe(III). The aqueous complexation of the polydentate ligands can be characterized mainly by formation of stable mononuclear 1 : 1 metal to ligand complex as the major species. This behavior is, as expected, equivalent to the complexation of the isomeric mixture of BCA6 [17]. In contrast to the isomeric mixture, a difference was found in the case of binuclear species, which were present in the isomeric mixture with Ca(II), Cu(II) and Zn(II). Equilibrium constants for these species (M_2HL^- for these three metal ions and M_2L^{2-} for Cu(II) and Zn(II)) could not be calculated for any metal ion with the [S,S,S]-isomer, nor with the [R,S,R]-isomer in the case of Zn(II), probably because of the very small amount of these species

Table 1. Protonation and complex formation of [S,S,S]-BCA6 and [R,S,R]-BCA6 with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II), and Zn(II) in aqueous 0.1 M NaCl at 25°C. (*only when $C_L \leq C_M$, χ^2/S 47.08/1.06, Points/Titrations 289/3).

p	q	r	$\log(\beta_{pqr} \pm 3\sigma)$ [S,S,S]-BCA6	$\log(\beta_{pqr} \pm 3\sigma)$ [R,S,R]-BCA6	$\log(\beta_{pqr} \pm 3\sigma)$ BCA6-mixture [17]	Formula
H^+						
−1	0	1	-9.38 ± 0.05	-8.99 ± 0.04	-8.98 ± 0.03	L^{6-}
1	0	1	5.58 ± 0.04	5.58 ± 0.04	5.47 ± 0.03	H_2L^{4-}
2	0	1	10.30 ± 0.03	10.29 ± 0.04	10.20 ± 0.02	H_3L^{3-}
3	0	1	14.32 ± 0.04	14.08 ± 0.05	14.16 ± 0.03	H_4L^{2-}
4	0	1	17.49 ± 0.04	17.09 ± 0.04	17.36 ± 0.03	H_5L^-
5	0	1	19.86 ± 0.05	19.31 ± 0.06	19.92 ± 0.05	H_6L
6	0	1	21.05 ± 0.18	20.48 ± 0.26	21.89 ± 0.06	H_7L^+
χ^2/S			11.90/0.82	9.62/0.82	51.19/0.85	
Points/Titrations			168/4	251/5	313/3	
Mg^{2+}						
−2	1	1	-14.30 ± 0.18	-13.64 ± 0.17	-14.07 ± 0.12	$Mg(OH)L^{5-}$
−1	1	1	-2.56 ± 0.11	-2.46 ± 0.13	-3.00 ± 0.06	MgL^{4-}
0	1	1	4.13 ± 0.09	4.00 ± 0.10	3.07 ± 0.08	$MgHL^{3-}$
1	1	1	9.22 ± 0.12	9.14 ± 0.13	7.99 ± 0.17	MgH_2L^{2-}
2	1	1	13.87 ± 0.09	13.58 ± 0.10	12.49 ± 0.14	MgH_3L^-
3	1	1	17.41 ± 0.18	17.06 ± 0.15	16.11 ± 0.50	MgH_4L
χ^2/S			24.00/1.60	25.50/2.10	35.78/1.25	
Points/Titrations			312/4	351/4	283/4	
Ca^{2+}						
−2	1	1	-11.91 ± 0.13	-11.26 ± 0.09	-11.27 ± 0.11	$Ca(OH)L^{5-}$
−1	1	1	-1.22 ± 0.10	-0.62 ± 0.08	-1.27 ± 0.03	CaL^{4-}
0	1	1	4.20 ± 0.11	4.51 ± 0.14	4.06 ± 0.04	$CaHL^{3-}$
1	1	1	8.97 ± 0.16	9.08 ± 0.19	8.47 ± 0.10	CaH_2L^{2-}
2	1	1	13.26 ± 0.15	13.33 ± 0.11	12.61 ± 0.10	CaH_3L^-
3	1	1	17.06 ± 0.16	16.98 ± 0.13	16.11 ± 0.32	CaH_4L
0	2	1		7.54 ± 0.30	6.03 ± 0.35	Ca_2HL^-
χ^2/S			15.38/1.81	27.79/1.03	12.10/0.92	
Points/Titrations			261/4	179/3	265/4	
Mn^{2+}						
−2	1	1	-10.25 ± 0.16	-8.48 ± 0.18	-10.79 ± 0.52	$Mn(OH)L^{5-}$
−1	1	1	0.72 ± 0.11	2.32 ± 0.13	0.30 ± 0.09	MnL^{4-}
0	1	1	5.59 ± 0.13	6.91 ± 0.12	5.56 ± 0.07	$MnHL^{3-}$
1	1	1	10.24 ± 0.15	10.87 ± 0.21	10.04 ± 0.08	MnH_2L^{2-}
2	1	1	14.01 ± 0.17	14.22 ± 0.17	13.56 ± 0.15	MnH_3L^-
3	1	1	17.58 ± 0.21	17.36 ± 0.40	16.52 ± 0.48	MnH_4L
χ^2/S			35.43/2.03	20.94/1.59	27.61/2.61	
Points/Titrations			263/4	215/4	372/4	
Fe^{3+}						
−2	1	1	0.10 ± 0.31	0.18 ± 0.33	2.66 ± 0.28	$Fe(OH)L^{4-}$
−1	1	1	7.79 ± 0.26	7.73 ± 0.26	8.32 ± 0.26	FeL^{3-}
0	1	1	12.85 ± 0.28	12.24 ± 0.29	12.65 ± 0.28	$FeHL^{2-}$
1	1	1	17.11 ± 0.27	16.27 ± 0.27	16.36 ± 0.26	FeH_2L^-
2	1	1	20.11 ± 0.28	18.44 ± 0.30	18.58 ± 0.30	FeH_3L
χ^2/S			20.37/1.57	12.01/1.08	18.67/0.96	
Points/Titrations			205/3	261/4	228/3	
Cu^{2+}						
−2	1	1	-5.18 ± 0.20	-5.61 ± 0.23	-5.91 ± 0.18	$Cu(OH)L^{5-}$
−1	1	1	5.21 ± 0.14	4.93 ± 0.20	4.10 ± 0.11	CuL^{4-}
0	1	1	9.44 ± 0.15	9.63 ± 0.19	8.90 ± 0.11	$CuHL^{3-}$
1	1	1	13.53 ± 0.15	13.79 ± 0.21	13.01 ± 0.12	CuH_2L^{2-}
2	1	1	16.53 ± 0.11	17.11 ± 0.17	16.34 ± 0.10	CuH_3L^-
3	1	1	19.47 ± 0.16	19.25 ± 0.27	18.99 ± 0.16	CuH_4L
−1	2	1		(7.84 ± 0.20)*	7.87 ± 0.12	Cu_2L^{2-}

(*Continued*)

Table 1. Continued.

p	q	r	$\log(\beta_{pqr} \pm 3\sigma)$ [S,S,S]-BCA6	$\log(\beta_{pqr} \pm 3\sigma)$ [R,S,R]-BCA6	$\log(\beta_{pqr} \pm 3\sigma)$ BCA6-mixture [17]	Formula
0	2	1		(12.16 ± 0.49)*	11.89 ± 0.17	Cu_2HL^-
χ^2/S			36.62/2.48	28.09/1.77	46.42/1.77	
Points/Titrations			467/6	402/6	285/4	
Zn^{2+}						
−2	1	1	-6.81 ± 0.14	-6.57 ± 0.09	-7.53 ± 0.39	$Zn(OH)L^{5-}$
−1	1	1	2.99 ± 0.07	3.53 ± 0.06	2.36 ± 0.05	ZnL^{4-}
0	1	1	7.31 ± 0.06	8.12 ± 0.07	7.25 ± 0.04	$ZnHL^{3-}$
1	1	1	11.09 ± 0.12	12.29 ± 0.06	11.42 ± 0.05	ZnH_2L^{2-}
2	1	1	14.28 ± 0.11	15.53 ± 0.03	14.92 ± 0.04	ZnH_3L^-
3	1	1	17.42 ± 0.26	17.68 ± 0.19	17.62 ± 0.12	ZnH_4L
−1	2	1			4.92 ± 0.30	Zn_2L^{2-}
0	2	1			9.62 ± 0.43	Zn_2HL^-
χ^2/S			18.42/1.81	47.20/1.66	81.10/2.04	
Points/Titrations			367/5	420/5	349/4	

or because their standard deviations were excessive. The species Ca_2HL^- was found for the [R,S,R]-isomer and the value of the stability constant is somewhat larger than for the isomeric mixture. For Cu(II) and the [R,S,R]-isomer, the binuclear species, Cu_2HL^- and Cu_2L^{2-}, were found only for situations where $C_L \leq C_M$ (χ^2/S: 47.08/1.06, points/titrations: 289/3). Obviously formation of binuclear species, which has been found for the isomeric mixture, must be favoured for some or all of the other isomers since they were not found with the [S,S,S]-isomer. The proposed formulas of the species, with the corresponding formation constants from equation (6) found in the equilibrium analysis of the different $H^+ - M^{n+} - HL^{5-}$ systems, are shown in table 1 and compared to corresponding values for the BCA6-mixture [17]. Comparison with the findings of earlier studies carried out with EDTA and DTPA [34] was facilitated by rewriting the complexation of [S,S,S]- and [R,S,R]-BCA6 with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II) and Zn(II) in the form given in table 2. The stability of the complexes follows the Irving-Williams order: $\log K_{MnL}(10.10) < \log K_{CuL}(14.59) > \log K_{ZnL}(12.37)$ for the [S,S,S]-isomer and $\log K_{MnL}(11.31) < \log K_{CuL}(13.92) > \log K_{ZnL}(12.52)$ for the [R,S,R]-isomer.

When the values of protonation constants or stability constants of metal complexes of [S,S,S] and [R,S,R] -BCA6 are compared, only minor differences can be found between the two isomers in most cases; the differences are often close to or within experimental errors. Both isomers form moderately strong ML^{n-6} complexes as the main species with all the metal ions studied here, and the values of these constants do not differ markedly. However, in the case of MnL^{4-}, the difference between the isomers is over one logarithm unit (the higher value for the [R,S,R]-isomer). For CuL^{4-}, a value about one logarithm unit higher is found for the [S,S,S]-isomer. For ZnL^{4-} and $Fe(OH)L^{4-}$, the differences between isomers and the BCA6-mixture, which has the lowest values, is about one logarithm unit. These two latter cases suggest that some unmeasured isomer would have an even lower value for those species than the isomeric mixture. On the other hand, differences can be found between the isomers in the case of binuclear species; the [S,S,S]-form seems to be unfavourable for binuclear complexes. Ca_2HL^- has a clearly higher value for the [R,S,R]-isomer than for the isomeric mixture. The differences between values of stabilities of the binuclear species Cu_2L^{2-} and Cu_2HL^- in the [R,S,R]-system compared to corresponding values for the BCA6-mixture were within experimental errors.

Table 2. Protonation and complexation of [S,S,S]-BCA6 and [R,S,R]-BCA6 with Mg(II), Ca(II), Mn(II), Fe(III), Cu(II), and Zn(II) compared to corresponding values of BCA6-mixture, EDTA and DTPA in $\mu = 0.1$ at 25°C ([a]at 37°C and in $\mu = 0.15$, [b]at 20°C, [c]in $\mu = 1.0$, *calculated from data, where $C_L \leq C_M$).

Reaction	[S,S,S]-BCA6 (H_6L) log K	[R,S,R]-BCA6 (H_6L) log K	BCA6-mix (H_6L) [17] log K	EDTA (H_4L) [34] log K	DTPA (H_5L) [34] log K
$L + H \leftrightharpoons HL$	9.38	8.99	8.98	9.52–10.37	9.90–10.79
$HL + H \leftrightharpoons H_2L$	5.58	5.58	5.47	6.13	8.40–8.60
$H_2L + H \leftrightharpoons H_3L$	4.72	4.71	4.73	2.69	4.28
$H_3L + H \leftrightharpoons H_4L$	4.02	3.79	3.96	2.00	2.70
$H_4L + H \leftrightharpoons H_5L$	3.17	3.01	3.20	(1.5)	2.0
$H_5L + H \leftrightharpoons H_6L$	2.37	2.22	2.56	(0.0)	(1.6)
$H_6L + H \leftrightharpoons H_7L$	1.19	1.17	1.97		(0.7)
$H_7L + H \leftrightharpoons H_8L$					(−0.1)
Mg(II)					
$M(OH)L + H \leftrightharpoons ML$	11.74	11.18	11.07		
$M + L \leftrightharpoons ML$	6.82	6.53	5.98	8.79	9.27
$ML + H \leftrightharpoons MHL$	6.69	6.46	6.07	4.0	6.85
$MHL + H \leftrightharpoons MH_2L$	5.09	5.14	4.92		
$MH_2L + H \leftrightharpoons MH_3L$	4.65	4.44	4.50		
$MH_3L + H \leftrightharpoons MH_4L$	3.54	3.48	3.62		
$ML + M \leftrightharpoons M_2L$					2.07[a]
Ca(II)					
$M(OH)L + H \leftrightharpoons ML$	10.69	10.64	10.00		
$M + L \leftrightharpoons ML$	8.16	8.37	7.71	10.65	10.75
$ML + H \leftrightharpoons MHL$	5.42	5.13	5.33	3.1	6.11
$MHL + H \leftrightharpoons MH_2L$	4.77	4.57	4.41		
$MH_2L + H \leftrightharpoons MH_3L$	4.29	4.25	4.14		
$MH_3L + H \leftrightharpoons MH_4L$	3.80	3.65	3.50		
$ML + M \leftrightharpoons M_2L$					1.6
$MHL + M \leftrightharpoons M_2HL$		3.03	1.97		
Mn(II)					
$M(OH)L + H \leftrightharpoons ML$	10.97	10.80	11.09		
$M + L \leftrightharpoons ML$	10.10	11.31	9.28	13.89	15.2
$ML + H \leftrightharpoons MHL$	4.87	4.59	5.26	3.1	4.45
$MHL + H \leftrightharpoons MH_2L$	4.65	3.96	4.48		
$MH_2L + H \leftrightharpoons MH_3L$	3.77	3.35	3.52		
$MH_3L + H \leftrightharpoons MH_4L$	3.57	3.14	2.96		
$ML + M \leftrightharpoons M_2L$					2.09[b]
Fe(III)					
$M(OH)L + H \leftrightharpoons ML$	7.69	7.55	5.66	7.39	9.66
$2\,M(OH)L \leftrightharpoons M_2(OH)_2L_2$				2.8[c]	
$M + L \leftrightharpoons ML$	17.17	16.72	17.30	25.1	28.0
$ML + H \leftrightharpoons MHL$	5.06	4.51	4.33	(1.3)	3.56
$MHL + H \leftrightharpoons MH_2L$	4.26	4.03	3.71		
$MH_2L + H \leftrightharpoons MH_3L$	3.00	2.17	2.22		
Cu(II)					
$M(OH)L + H \leftrightharpoons ML$	10.39	10.54	10.01	(11.4)	
$M + L \leftrightharpoons ML$	14.59	13.92	13.08	18.78	21.2
$ML + H \leftrightharpoons MHL$	4.23	4.70	4.80	3.1	4.80
$MHL + H \leftrightharpoons MH_2L$	4.09	4.16	4.11	2.0	2.96
$MH_2L + H \leftrightharpoons MH_3L$	3.00	3.32	3.33		
$MH_3L + H \leftrightharpoons MH_4L$	2.94	2.14	2.65		
$ML + M \leftrightharpoons M_2L$		(3.5)*	3.77		6.79
$MHL + M \leftrightharpoons M_2HL$		(2.6)*	2.99		
Zn(II)					
$M(OH)L + H \leftrightharpoons ML$	9.80	10.10	9.89	(11.6)	
$M + L \leftrightharpoons ML$	12.37	12.52	11.34	16.5	18.2

(*Continued*)

Table 2. Continued.

Reaction	[S,S,S]-BCA6 (H_6L) log K	[R,S,R]-BCA6 (H_6L) log K	BCA6-mix (H_6L) [17] log K	EDTA (H_4L) [34] log K	DTPA (H_5L) [34] log K
$ML + H \leftrightharpoons MHL$	4.32	4.59	4.89	3.0	5.60
$MHL + H \leftrightharpoons MH_2L$	3.78	4.17	4.17	(1.2)[c]	
$MH_2L + H \leftrightharpoons MH_3L$	3.19	3.24	3.50		
$MH_3L + H \leftrightharpoons MH_4L$	3.14	2.15	2.70		
$ML + M \leftrightharpoons M_2L$			2.56		4.48
$MHL + M \leftrightharpoons M_2HL$			2.37		

The values of the stability constants of acidic complexes, MH_iL^{n-6+i}, can also be compared by rewriting them in terms of the formation of protonated complexes from the form of the ligand with the same number of protons, instead of the proton association reactions, as described in equations (8)–(11) (charges are omitted for clarity).

$$M + HL \rightleftharpoons MHL \quad K_{MHL} = \frac{MHL}{M \cdot HL} \tag{8}$$

$$M + H_2L \rightleftharpoons MH_2L \quad K_{MH_2L} = \frac{MH_2L}{M \cdot H_2L} \tag{9}$$

$$M + H_3L \rightleftharpoons MH_3L \quad K_{MH_3L} = \frac{MH_3L}{M \cdot H_3L} \tag{10}$$

$$M + H_4L \rightleftharpoons MH_4L \quad K_{MH_4L} = \frac{MH_4L}{M \cdot H_4L} \tag{11}$$

This allows a direct comparison of the tendencies of the protonated forms of ligands to form corresponding protonated complexes. Although the differences are in most cases small, some trends can still be seen, as shown in table 3. The $\log K_{MH_iL}$ values of all protonated complexes are somewhat higher for the [S,S,S]-isomer than for the [R,S,R]-isomer in the case of Mg(II) and Fe(III) ions. For Ca(II), Mn(II), Cu(II) and Zn(II) ions, the [R,S,R]-isomer has, in contrast, higher values than the [S,S,S]-isomer, suggesting some structural factor related e.g. to the ion size, which makes the [S,S,S]-isomer favourable in the case of the smaller ions and the [R,S,R]-isomer favourable for the larger ions. Another interesting observation is that order of magnitude of $\log K_{MHiL}$ for Ca(II) and Mg(II) ions changes with increasing degree of protonation. This trend seems to be stronger for the [S,S,S]-isomer than for the [R,S,R]-isomer.

The dominant role of ML^{n-6} complexes over a wide pH range in solutions, where the metal-to-ligand ratio is 1 : 1, as well as the effect of stereoselectivity, is illustrated in figure 3, showing the percentage distribution of the metals among different complex species as a function of pH in the millimolar concentration range ($C_M = C_L = 1\,mM$, where C_L consists of equal amounts of [S,S,S]- and [R,S,R]-isomers). It can be concluded that, in dilute solution, both isomers are effective chelating agents. The small difference between the isomers is not significant from the point of view of the strength in chelating capability. The binary hydrolysis of Fe(III) is very strong and the presence of the various $Fe(OH)_x^{3-x} (x = 1-4)$ species in solution is markedly increased by dilution.

Table 3. Comparison of log *K* values of acidic complex species expressed as combining metal ions directly with H_iL (as defined in equations (8)–(11)).

M	[S,S,S]-BCA6 MHL	[S,S,S]-BCA6 MH_2L	[S,S,S]-BCA6 MH_3L	[S,S,S]-BCA6 MH_4L	[R,S,R]-BCA6 MHL	[R,S,R]-BCA6 MH_2L	[R,S,R]-BCA6 MH_3L	[R,S,R]-BCA6 MH_4L
Mg(II)	4.13	3.64	3.57	3.09	4.00	3.56	3.29	2.98
Fe(III)	12.85	11.53	9.81	–	12.24	10.69	8.15	–
Ca(II)	4.20	3.39	2.96	2.74	4.51	3.50	3.04	2.90
Mn(II)	5.59	4.66	3.71	3.26	6.91	5.29	3.93	3.28
Cu(II)	9.44	7.95	6.23	5.15	9.63	8.21	6.82	5.17
Zn(II)	7.31	5.51	3.98	3.10	8.12	6.71	5.24	3.60

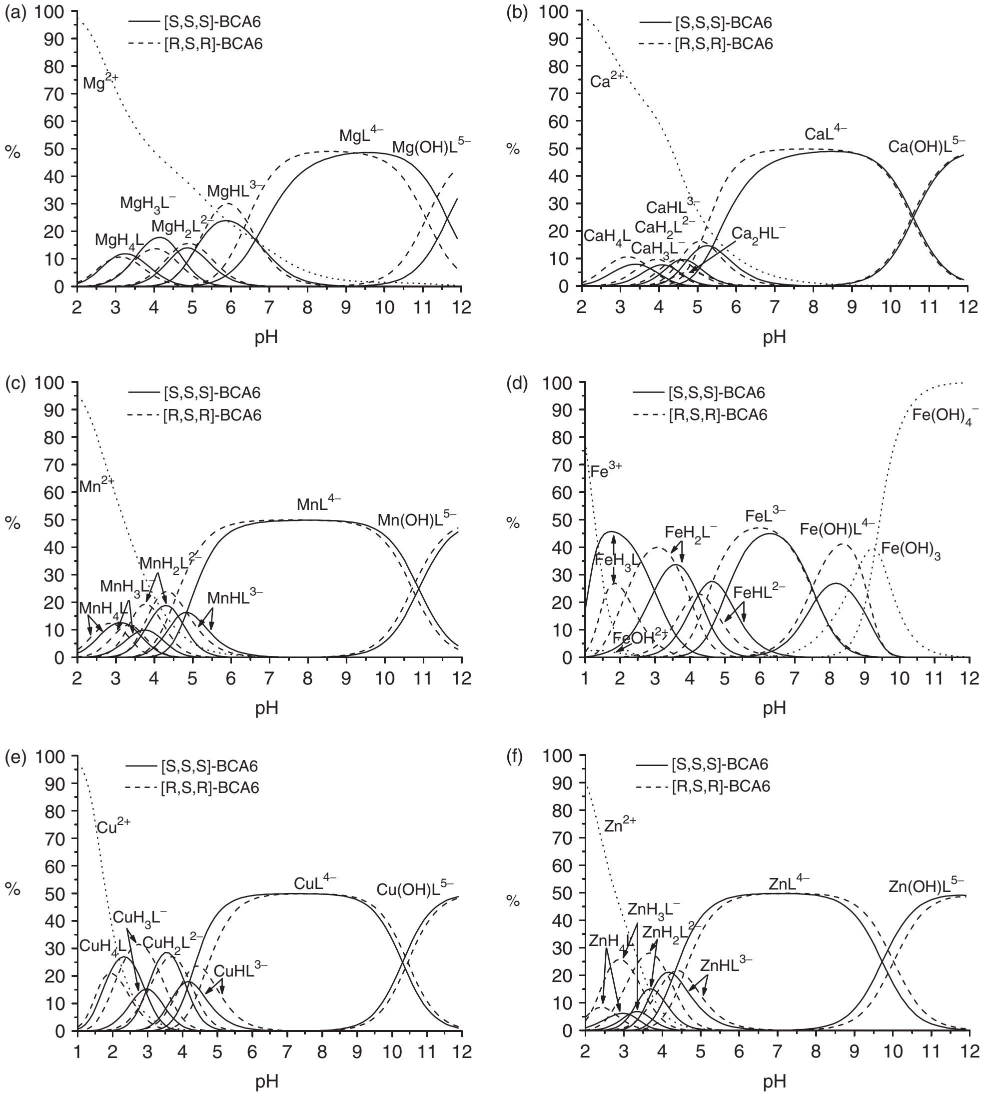


Figure 3. Percentage distribution of the different (a) Mg(II), (b) Ca(II), (c) Mn(II), (d) Fe(III), (e) Cu(II) and (f) Zn(II) complexes of [S,S,S]-BCA6 and [R,S,R]-BCA6 as a function of pH.

The stabilities of the metal chelates of BCA6 are somewhat lower than those of EDTA and DTPA. On the other hand, BCA6 shows greater biodegradability than EDTA and DTPA (OECD 301B –test and ISO9439 –test) [25–27]. The photodegradability of BCA6 has also been reported [28]. Additionally, BCA6 has proved its superiority compared to EDTA in terms of degradability by Fenton's process [29]. These aspects make BCA6 less harmful to the environment than EDTA and DTPA. Although the strength of complexation of Mn(II) and Fe(III) ions, which is important in pulp bleaching, is lower than that of EDTA and DTPA, it appears to be great enough for practical applications. More importantly, the Mn-BCA6 complexes appear to be inert in hydrogen peroxide and peracetic acid solution, whereas Mn-EDTA and Mn-DTPA complexes are capable of decomposing the peroxy compounds. Use of BCA6 is also environmentally advantageous as it leads to a reduction in chemical use and process steps [17]. In addition, its substantially lower nitrogen content compared to EDTA and DTPA makes BCA6 an environmentally friendly chelating agent in pulp bleaching. The results of this study show that [S,S,S] and [R,S,R] isomers of BCA6 are both effective chelating agents. From the environmental perspective, it would be important to determine whether the biodegradability of the isomers of BCA6 differs significantly, as in the case of EDDS.

References

[1] D. Williams. *Chem. Br.*, **34**, 48 (1998).
[2] T.P. Knepper. *Trend. Anal. Chem.*, **22**, 708 (2003).
[3] B. Nowack. *Environ. Sci. Technol.*, **36**, 4009 (2002).
[4] M. Fuerhacker, G. Lorbeer, R. Haberl. *Chemosphere*, **52**, 253 (2003).
[5] A.-S. Allard, L. Renberg, A.H. Neilson. *Chemosphere*, **33**, 577 (1996).
[6] V. Sýkora, P. Pitter, I. Bittnerová, T. Lederer. *Wat. Res.*, **35**, 2010 (2001).
[7] J.L. Means, T. Kucak, D.A. Crerar. *Environ. Poll. (Ser. B)*, **1**, 45 (1980).
[8] M. Sillanpää. *Rev. Environ. Contam. Toxicol.*, **152**, 85 (1997).
[9] F.G. Kari, W. Giger. *Wat. Res.*, **30**, 122 (1996).
[10] V. Hornburg, G.W. Brümmer. *Z. Pflanzenernähr. Bodenk.*, **156**, 467 (1993).
[11] B. Nowack, F.G. Kari, H.G. Krüger. *Water, Air Soil Poll.*, **125**, 243 (2001).
[12] ECB, European Chemical Bureau. *European Union risk assessment report, tetrasodiumethylenediaminetetraacetate*, 51, (2004).
[13] R. Aksela, A. Parén, J. Jäkärä, I. Renvall. Application of ethylenediamine disuccinic acid and iminodisuccinic acid as biodegradable chelating agents in pulp bleaching, *4th International Conference on Environmental Impacts of the Pulp and Paper Industry*, Helsinki, Finland, p. 340, June 12–15 (2000).
[14] J. Jäkärä, A. Parén, I. Renvall, R. Aksela. Peracetic acid in low AOX and high brightness pulp production, *Japan Tappi Annual Meeting*, Nagoya, Japan, November 10–14 (1997).
[15] A. Parén, R. Aksela, J. Jäkärä, I. Renvall. Study of the effect of new alternative complexing agents on peroxide and peracetic acid bleaching, *6th European Workshop on Lignocellulosics and Pulp*, Bordeaux, France, p. 503, September 3–6 (2000).
[16] R. Aksela, A. Parén, J. Jäkärä, I. Renvall. The overall performance of new diethanolamine derivatives as complexing agents in peroxide and peracetic acid bleaching of TCF pulp, *11th ISWPC International Symposium on Wood and Pulping Chemistry*, p. 481, Nice, France, June 11–14 (2001).
[17] H. Hyvönen, M. Orama, R. Arvela, K. Henriksson, H. Saarinen, R. Aksela, A. Parén, J. Jäkärä, I. Renvall. *Appita J.*, **59**, 142 (2006).
[18] H. Hyvönen, M. Orama, P. Alén, H. Saarinen, R. Aksela, A. Parén. *J. Coord. Chem.*, **58**, 1115 (2005).
[19] M. Orama, H. Hyvönen, H. Saarinen, R. Aksela. *J. Chem. Soc. Dalton Trans.*, 4644 (2002).
[20] H. Hyvönen, M. Orama, H. Saarinen, R. Aksela. *Green Chem.*, **5**, 410 (2003).
[21] H. Hyvönen, R. Aksela. *J. Coord. Chem.*, **60**, 901 (2007).
[22] H. Hyvönen, P. Lehtinen, R. Aksela R. *J. Coord. Chem.*, accepted.
[23] Z. Yuan, M. d'Entremont, Y. Ni, A.R.P. van Heiningen. *Pulp & Paper Canada*, **98**(11), T408 (24) (1997).

[24] D. Schowanek, T.C.J. Feijtel, C.M. Perkins, F.A. Hartman, T.W. Federle, R.J. Larson. *Chemosphere*, **34**, 2375 (1997).

[25] S. Metsärinne, E. Ronkainen, T. Tuhkanen, R. Aksela, M. Sillanpää. *Sci. Total Environ.*, **377**, 45 (2007).

[26] S. Metsärinne. Degradation of novel and conventional complexing agents. PhD thesis, University of Kuopio, Finland (2006).

[27] M. Itävaara, M.Vikman. Research Report BEL 235/97, Technical Research Centre of Finland, Espoo (1997).

[28] S. Metsärinne, P. Peltonen, R. Aksela, T. Tuhkanen. *Chemosphere*, **56**, 1077 (2004).

[29] K. Pirkanniemi, S. Metsärinne, M. Sillanpää. *J. Hazard. Mater.*, **147**, 556 (2007).

[30] J. Jäkärä, R. Aksela. *Pulp & Paper International*, **48**, 28 (2006).

[31] P.M. Pihko, T.K. Rissa, R. Aksela. *Tetrahedron*, **60**, 10949 (2004).

[32] C.F. Baes, R.E. Mesmer. *The Hydrolysis of Cations*, Wiley, New York (1976).

[33] P. Gans, A. Sabatini, A. Vacca. *J. Chem. Soc. Dalton Trans.*, 1195 (1985).

[34] A.E. Martell, R.M. Smith. *Critical Stability Constants Database*, NIST, Gaithersburg, MD, USA (2003).