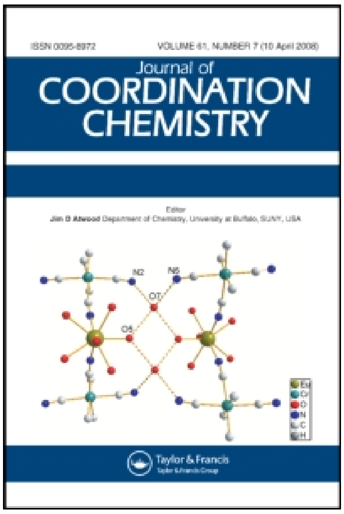

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POTENTIOMETRIC, POLAROGRAPHIC AND SPECTROSCOPIC STUDIES OF THE Cu(II)-D-GLUCOSAMINE-D-LACTOBIONIC ACID TERNARY SYSTEMS

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NOTE

POTENTIOMETRIC, POLAROGRAPHIC AND SPECTROSCOPIC STUDIES OF THE Cu(II)-*D*-GLUCOSAMINE-*D*-LACTOBIONIC ACID TERNARY SYSTEMS

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Our recent work on Cu(II) and VO(IV) interactions with lactobionic acid have shown[1,2] that this sugar acid has an unusually high ability to coordinate both metal ions. The carboxyl group is not a very effective donor for cupric ions[3,4] and metal interations with the set of the protonated hydroxyl groups should have considerable effects on complex stability. This high stability of the lactobionic acid complexes can lead to the involvement of this ligand in formation of ternary complexes with ligands such as aminosugars.[3–6] Both ligands are important chelating agents for Cu(II) ions in medicine, agriculture and food chemistry.[7–9] Since ternary complexes may play an important role in natural systems we have decided to follow complex formation in solutions containing lactobionic acid and one an aminosugar, *D*-glucosamine. The anchoring group in *D*(+)-glucosamine (2-amino-2-deoxy-*D*-glucose) is an amino group which is much more effective donor than carboxylate which acts as an anchor in sugar acids. Thus in our study we have used excess lactobionic acid to promote the formation of ternary complexes as major species in the solutions studied.

KEY WORDS: Copper(II), glucosamine, lactobionic acid, complexes, stability constants.

EXPERIMENTAL

Potentiometric titrations were carried out using a Tacussel Isis 2000 pH meter with a TG 100 glass electrode at 25±0.03°C for the 1:1:7 Cu(II): *D*-glucosamine (GlcN): *D*-lactobionionc acid (LacA) molar ratio. All solutions were prepared under argon atmosphere in deionized and bi-distilled water. "Puratronic" culpric chloride was dissolved in HCl solution to obtain 0.129 mol dm^{-3} of metal (checked with EDTA and spectrophotometry). D(+)-Glucosamine hydrochloride (Fluka) and D-lactobionic acid (Jensen Chimica) were used as obtained. Stock solutions of ligands were prepared in 0.1 M KNO_3. The purity of the ligands was evaluated by the Gran method.[10] Stability constants were calculated with the SUPERQUAD computer program[11] adapted for an IBM-PC microcomputer.

EPR measurements were carried out on a Varian E 109 spectrometer at 9.3 GHz, at 77 K. CD spectra were recorded on a Jobin-Yvon Mark III spectropolarimeter. For spectroscopic measurements metal concentration was 5×10^{-3} mol dm^{-3} while in the potentiometric study it was 10^{-3} mol dm^{-3}.

Polarographic measurements were carried out on a Radelkis OH-105 polarograph with a dropping mercury electrode (dropping time 4.05 s). All measurements were performed at 25°C in a medium of constant ionic strength (0.5 M, $NaClO_4$). The experiments were carried out under argon. The concentration of metal was adjusted to 5×10^{-5} mol dm^{-3}.

RESULTS AND DISCUSSION

In the acidic region, lactobionic acid undergoes the lacton-acid reaction which drastically influences coordination and especially the potentiometric measurements; our procedure was as presented earlier.[1]

Potentiometric data presented in Table 1 clearly indicate the formation of ternary complexes under the conditions used in this experiment. Two binary complexes with LacA are formed in the acidic pH range. At low pH the carboxylate group ($pK = 3.53$) is a more effective anchor than the amino group ($pK = 7.57$). However, at pH above 4.5 the major complexes formed are the mixed species which become major complexes at a pH above 6.0.

Table 1 Stability constants (logβ) of proton and Cu(II) complexes with D(+)-glucosamine and D-lactobiobionic acid and the Cu(II) ternary complexes with GlcN and LacA at 25°C and 0.1 M KNO_3

Cu(II)	LacA L	GlcN L′	H	log β	dominant species at pH
0	1	0	1 (LH)	3.531[a]	
0	0	1	1(L′H)	7.57[b]	
1	1	0	0 (CuL)	3.10 (0.03)[c]	
1	2	0	0 (CuL_2)	5.90 (0.04)	4.5
1	2	0	−1 (CuL_2H_{-1})	−0.43 (0.02)	
1	2	0	−2 (CuL_2H_{-2})	−7.05 (0.07)	
1	0	2	0 (CuL'_2)	9.02[d]	
1	0	2	−2 (CuL'_2H_{-2})	−5.26[d]	
1	1	1	0 (CuLL′)	8.16 (0.15)	6.8
1	1	1	−1 ($CuLL'H_{-1}$)	2.28 (0.02)	
1	1	1	−2 ($CuLL'H_{-2}$)	−5.18 (0.03)	7.6
1	1	1	−3 ($CuLL'H_{-3}$)	−13.14 (0.03)	>8.5

[a] Ref.[1].
[b] Refs.[12,13].
[c] For the stabilities obtained in this work the standard deviations are given in parentheses.
[d] Ref.[13].

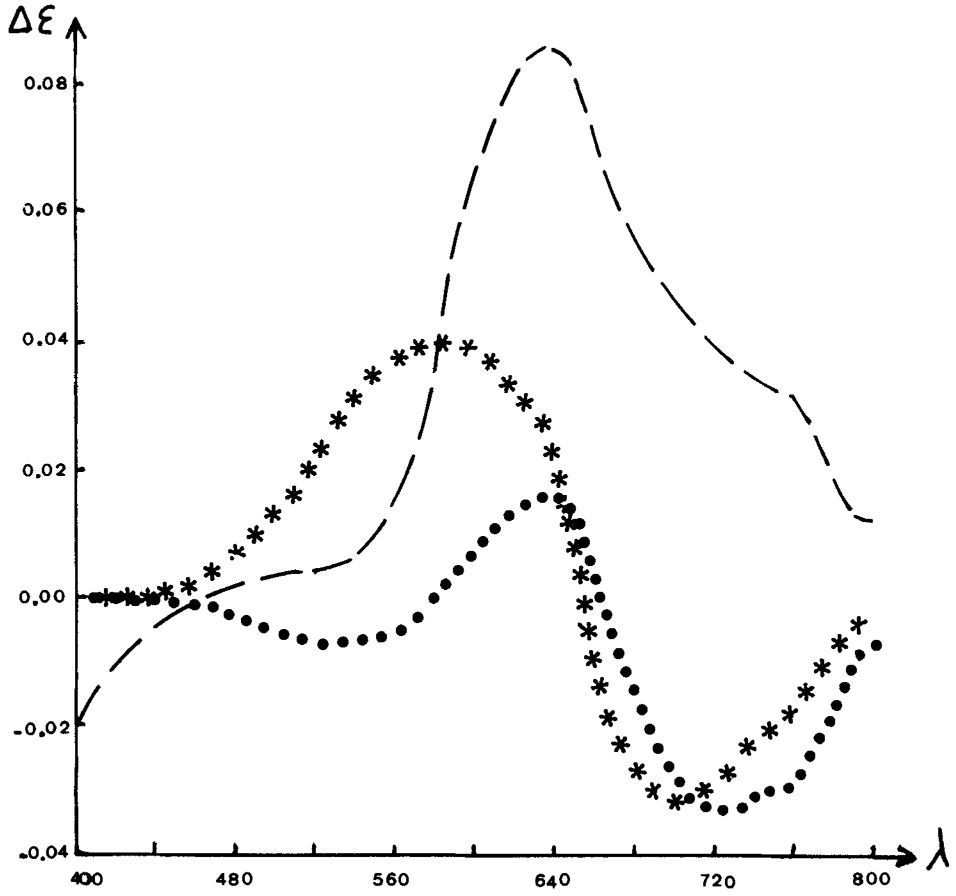

Figure 1 Visible region of CD spectra for Cu(II)-LacA (---), Cu(II)-GlcN (···) and Cu(II)-GlcN-LacA (****) systems at pH 10.8.

Since potentiometric titrations indicated the formation of ternary systems, EPR and CD spectra were used to obtain additional data to identify them. Spectroscopic descriptions of binary Cu(II) complexes with GlcN and LacA were presented earlier.[1,12] CD results attributed to binary complexes are distinctly different to those obtained for mixed species as is seen in the example given in Figure 1. Thus, potentiometric as well as spectroscopic data strongly suggest that the ternary complexes are formed, but only when an excess of lactobionic acid is used. Binding modes in these complexes can be deduced from the spectroscopic parameters as well as from discussion reported earlier[1,12] for binary systems. Coordination sites proposed are collected in Table 2. Deprotonation of a ligand hydroxyl group is assumed to begin on LacA ligand as is the case in the binary complexes (at lower pH than for GlcN[1,12]). Binding of amino and sugar hydroxyl group to cupric ion is supported by two distinct CD bands observed in the charge-transfer region for the respective donors (Table 2).[1,12]

Table 2 Spectroscopic parameters for the Cu(II) ternary complexes with LacA and GlcN ligands. Only the major species are taken into account. The parameters of the CD spectra were calculated from the spectrum at pH at which according to potentiometric data the maximum concentration of the respective complex was observed

Species	CD λ[nm], ($\Delta\varepsilon$)	EPR $g_{\parallel}$	$A_{\parallel}$ [10^{-4} cm^{-1}]	Suggested coordination mode {L}, {L'}
CuL	694 (-0.12)[a]	2.364	138	{COO^-}
CuL_2	774 (-0.03)[a] 650 ($+0.02$)[a]			
$CuLL'H_{-1}$	782 (-0.001)[a] 652 ($+0.014$)[a] 576 (-0.004)[a] 516 ($+0.003$)[a] 332 (-0.70)[b] 290 ($+0.25$)[c]	2.302	170	{COO^-,O^-}, {NH_2}
$CuLL'H_{-2}$	709 (-0.018)[a] 607 ($+0.021$)[a] sh558 ($+0.017$)[a] 315 (-0.30)[b] 280 ($+0.50$)[c]	2.268	182	{COO^-,O^-}, {NH_2,O^-}
$CuLL'H_{-3}$	703 (-0.032)[a] 584 ($+0.040$)[a] 312 (-0.33)[b] 260 ($+0.60$)[c]	2.258	189	{O^-,O^-}, {NH_2,O^-}

[a] d-d Transitions.

[b] $NH_2 \Rightarrow CU^{2+}$ charge-transfer transition, (ref. [12]).

[c] $O^- \Rightarrow Cu^{2+}$ charge-transfer transition (ref. [1]); absorption coefficients in $M^{-1}cm^{-1}$.

Further independent evidence for the ternary complexes in Cu(II)-LacA-GlcN solutions in the pH range 6–10 was obtained from polarographic measurements. The reduction waves of metal ion in binary systems are very characteristic for both studied ligands (e.g., for pH 6.57 see Figure 2). Formation of binary chelate complexes with LacA leads to a strong shift of the reduction waves towards more negative potentials and a multicomponent curve is observed. The reduction wave of mixed-ligand system is a single well-shaped curve and is distinctly shifted from that of the GlcN complex towards more negative potentials (Figure 2). This strongly supports formation of mixed complexes in the studied system in which reduction of the metal ion differs distinctly from that observed in both binary solutions.

Thus, lactobionic acid is a competitive ligand even for potent chelators such as those containing amino nitrogen atoms.

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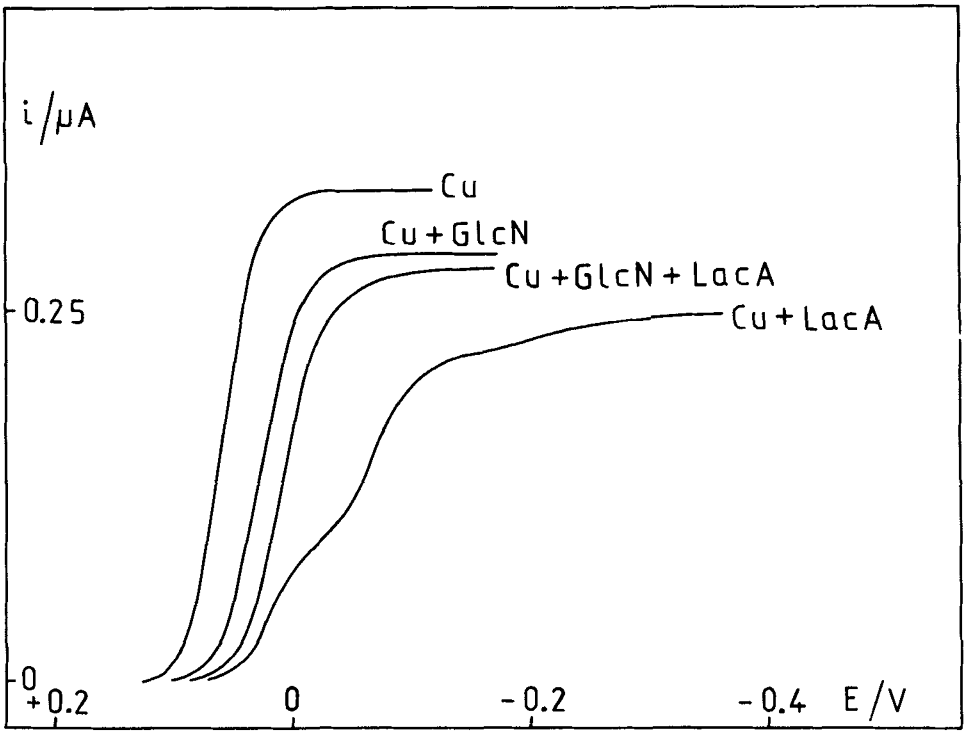

Figure 2 Polarograms for Cu(II)-aquaion, Cu(II)-GlcN, Cu(II)-LacA and Cu(II)-GlcN-LacA solutions at pH 6.57; $[\mathrm{Cu}]=5\times10^{-5}$, $[\mathrm{GlcN}]=2\times10^{-3}$ and $[\mathrm{LacA}]=10^{-2}$ mol dm^{-}3.

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