Potentiometric and Spectroscopic study of Copper(II), Nickel(II) and Cobalt(II) Complexation by Methoxy-D-glucosamine

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Our recent studies on the complexation of metal ions by D-glucosamine [1, 2] have shown that an amino sugar is quite an effective ligand for some transition metal ions, especially for cupric ions. Also Ni(II) and Co(II) form effective complexes with amino sugar ligands, especially the ML_2H_{-2} species in which the metal ion is chelated by (NH_2, O^-) donor sets [2].

The potentiometric data obtained for the cupric system suggested that in the high pH region (above 8) a further deprotonation process took place and the formation of CuL_2H_{-3} was established. The deprotonation of the apically bound water molecule was assumed. This assumption, however, seems to be doubtful especially when similar complexes with, e.g., amino acids or peptides are compared [3]. The other possibility for the deprotonation is one of hydroxyl groups of a bound ligand molecule, different from that directly involved in metal ion binding at the C1 position [1]. In order to check this possibility we have prepared the methoxy derivative of D-glucosamine (at the C1 position) and have carried out a potentiometric and spectroscopic study of its complexation with Cu(II) as well as with Ni(II) and Co(II) ions.

Experimental

The preparation of 1-methoxy-D-glucosamine was carried out as described earlier [4]. Its purity was checked by gas chromatography and mass spectrography and showed that 99.9% of D-glucosamine was methylated at the C1 position.

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The potentiometric titrations were performed on a Tacussel ISIS 200 pH-meter at 25 °C with a TB 10/HA glass electrode and a KCl saturated reference electrode. The other experimental details have been described earlier [2]. The calculations of the stability constants were carried out with a SUPERQUAD program [5]. Absorption spectra were recorded on a Beckman Acta 7 spectrophotometer and CD spectra on a Jobin–Yvon Mark III spectropolarimeter for the solutions with metal concentrations 2 mM and a 5-fold excess of ligand. The $\Delta\epsilon = (\epsilon_l - \epsilon_r)$ were calculated for the total concentration of metal ion in solution.

ESR spectra were recorded on a Varian E-9 spectrometer at 9.15 GHz and at 120 K.

The quantities of copper, nickel and cobalt, as well as the ligand used in titrations, are given in Table I.

Table I. Quantity of Metal and Ligand used in the Titrations (μ mol) (the number of titrations are given in parantheses)

Metal	1-Methoxy-D-glucosamine		
Cu(II)			
0	20.15(2)	26.8(2)	34.0(3)
6		26.8(2)	
10	20.15(2)	26.8(2)	34.0(2)
14		26.8(2)	34.2(2)
Ni(II)			
2.26		38.5(1)	
4.48	29.0(1)	38.5(1)	48.2(1)
8.95		38.5(1)	
Co(II)			
1.05		38.5(1)	
2.10	29.0(1)	38.5(1)	48.2(1)
4.20		38.5(1)	

Results and Discussion

The protonation constant of methoxy-D-glucosamine is almost identical to that obtained for D-glucosamine [1]. The Cu(II) stability constants obtained for both ligands are, however, distinctly different (Table II). The species distribution (Fig. 1), indicates that two major complexes observed in the Cu(II)–methoxy-D-glucosamine containing system, *i.e.* CuL (110), and CuL_2H_{-1} (12–1), were not found by SUPERQUAD calculations in the Cu(II)–D-glucosamine solutions [2], although they were found by the F.I.C.S. (Free Ionization Concentration of Species) calculations as a minor species. The formation of three major species in the Cu(II)–methoxy-D-glucosamine solutions is clearly indicated by the

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Table II. Logarithms or Stability Constants of Cupric Complexes in 0.15 M NaCl at 25 °C and the Respective Spectroscopic Data

$M_p L_q H_r$	log β_{pqr}	CD spectra		EPR spectra	
		λ (nm)	Δε	$g_{\|\|}$	$A_{\|\|}$ (gauss)
0 1 1 (LH)	7.689(0.009)[a] [7.700][b]				
1 1 0 (CuL)	4.126(0.016)	765(A)[c]	−0.02	2.341	135.0
		645(B)	+0.035		
		535(E)	−0.010		
		290(CT)[d]	−0.7		
1 2 0 (CuL_2)	7.52(0.09) [9.02]				
1 2 −1 (CuL_2H_{-1})	1.384(0.006)	725(A)	−0.02	2.245	183.0
		605(B+E)	+0.05		
		283(CT)	−0.8		
1 2 −2 (CuL_2H_{-2})	−6.847(0.03) [−5.82]	710(A)	−0.03	2.239	190.0
		585(B)	+0.07		
		470(E)	+0.03		
		270(CT)	−1.5		

[a]Standard deviations. [b]Log β_{pqr} for respective species in the Cu–D-glucosamine system [2]. [c]A, B and E are the d–d transitions (see e.g. ref. 3). [d]$NH_2 \rightarrow$ Cu(II) charge-transfer transition (see ref. 1).

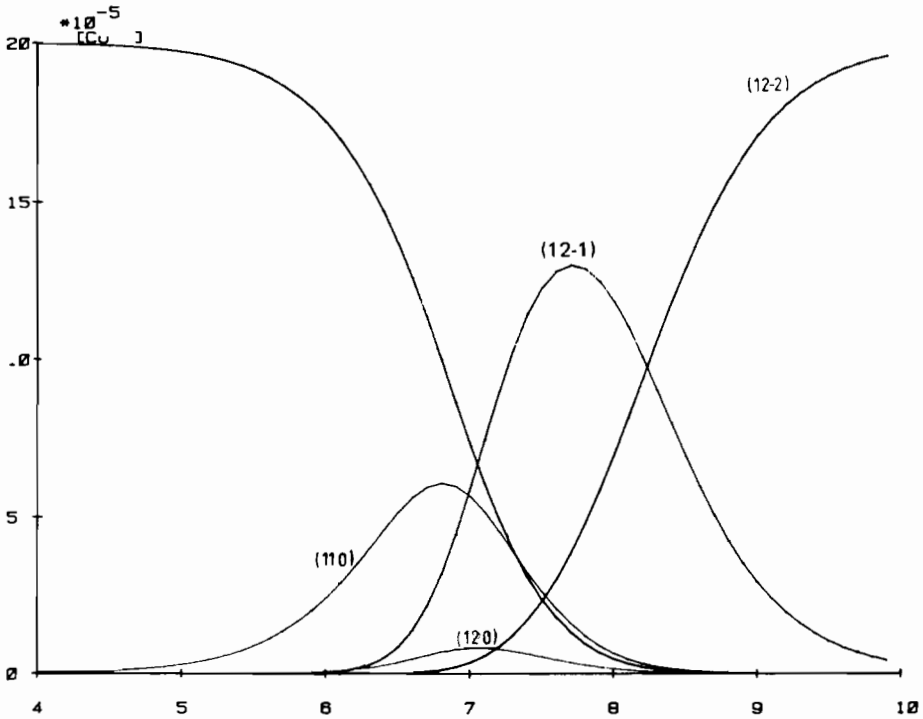

Fig. 1. The species distribution for the Cu(II)–methoxy-D-glucosamine solution with the 1:2.68 metal to ligand molar ratio.

spectroscopic data (Table II). Only one of them is a major complex for both ligands, *i.e.* (1 2 −2) or CuL_2H_{-2}, in which the ligand molecule binds the metal ion via an $\{NH_2, O^-\}$ donor set. The hydroxyl oxygen bound to the metal ion in a D-glucosamine-containing complex is probably derived from the C1–OH group which is blocked in the methoxy derivative. Thus in the latter case, the oxygen donor may be derived from the C3–OH or C4–OH group. The 5- and 6-membered chelate rings could also be formed.

Chelate formation with the use of C3–OH may distinctly affect the planarity of the cupric complex since both donors, according to the molecular model, show considerable hindrance when placed in the planar mode of metal ion coordination. The formation of a 6-membered chelate ring with amino- and C4-oxygen donors seems to be sterically more favourable. The latter mode of coordination could introduce, however, more effective interligand repulsions in the CuL_2 complex. This may explain the formation of the 1:1 species as a major complex in the lower pH region in the system studied here. In the Cu(II)–D-glucosamine system the {NH_2, Cl–OH} chelation keeps the sugar ring in a pseudo-equatorial position, *i.e.* far away from other species (CuL_2 or CuL_{-2}). The same situation could be expected for {NH_2, C3–OH} chelation. The involvement of the C4-oxygen in the chelate formation needs the sugar ring to be placed in an axial position with respect to the complex plane and this will make the formation of a CuL_2 complex less favourable.

No CuL_2H_{-3} species was found in the system considered in this work. This result could indicate that a deprotonation process which in the Cu(II)–D-glucosamine system was assigned as a proton release from an apically bound water [1], is more likely to be derived from the hydroxyl group of a ligand molecule; e.g. C4–OH may interact apically with the metal ion in the CuL_2H_{-2} complex in which the {NH_2, Cl–O^-} donor set is bound in the equatorial position. This interaction is sterically possible and it may promote the hydroxyl deprotonation.

The complex equlibria in Ni(II) and Co(II) with the methoxy derivative are also considerably different from those found with D-glucosamine (Table III, Figs. 2 and 3). Again the equimolar species (110), as in the case of cupric ions, is a major product (about 30% of bound metal ion) in the lower pH region. This complex could not be found in the D-glucosamine-containing solutions [2]. Neither Ni(II) nor Co(II) form (120) complex species with methoxyglucosamine, although it was the major species

Table III. Logarithms of Stability Constants of Ni(II) and Co(II) Complexes with 1-Methoxy-D-glucosamine (Metgluc) and D-Glucosamine (Gluc) in 0.15 M NaCl at 25 °C (standard deviations are given in parentheses)

$M_p L_q H_r$ species	log β_{pqr}			
p q r	Ni(II)		Co(II)	
	Metgluc	Gluc [2]	Metgluc	Gluc [2]
1 1 0	3.10(0.03)		2.93(0.01)	
1 2 0		6.73		
1 2 –1	–2.59(0.01)		–1.945(0.004)	
1 2 –2	–12.13(0.02)	–12.13	–10.77(0.009)	–12.20

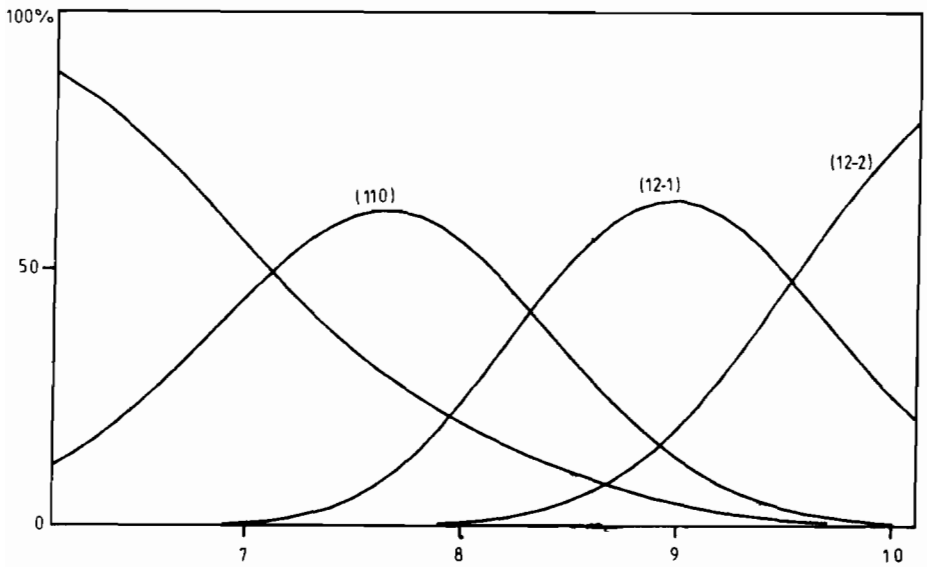

Fig. 2. The species distribution for the Ni(II)–methoxy-D-glucosamine solution with the 1:8.59 metal to ligand molar ratio.

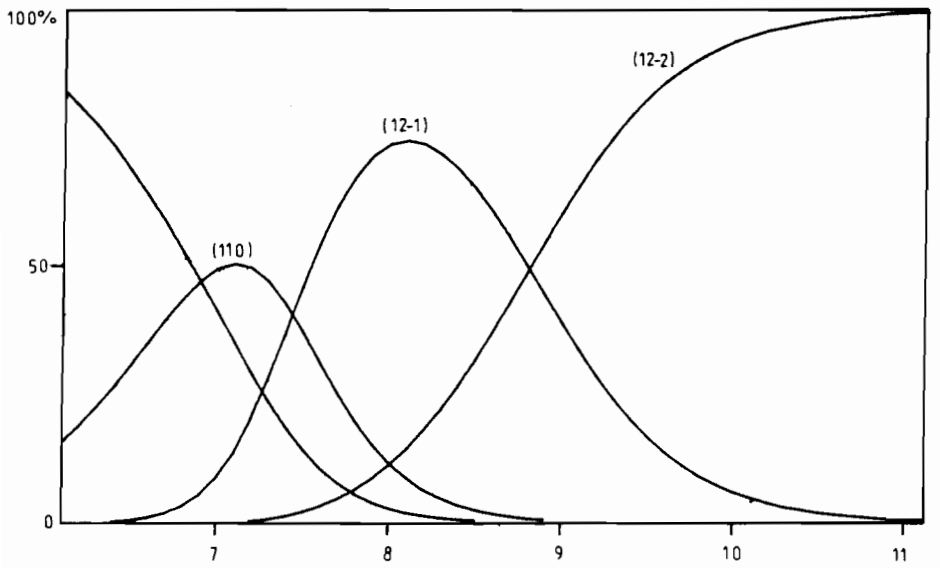

Fig. 3. The species distribution for the Co(II)–methoxy-D-glucosamine solution with the 1:18.33 metal to ligand molar ratio.

in Ni(II)–D-glucosamine solutions in the pH region 8–9 [2]. The formation of a 1:2 molar ratio species is possible only when at least one of the ligand hydroxyl groups undergoes the deprotonation process yielding a (1 2 –1) or (1 2 –2) complex. These results clearly indicate that in the case of D-glucosamine the C1–OH donor is a binding site and its blocking drastically changes the coordination mode of the amino sugar ligand. The similar behaviour of all three metal ions in their interaction with the methoxy derivative indicates that the binding modes between 1-methoxy-D-glucosamine and Ni(II) and Co(II) are similar to those described above for cupric ions; *i.e.* the $\{NH_2, C4–O^-\}$ donor set is a basic binding site in amino sugar derivatives.

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