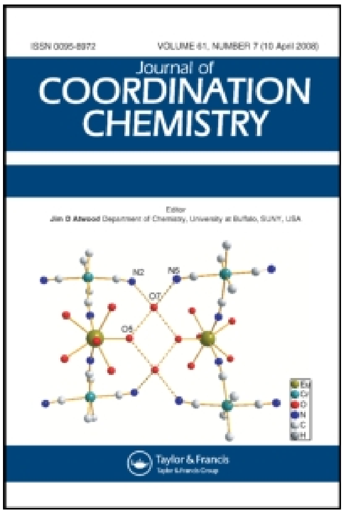

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POLAROGRAPHIC STUDIES OF COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES WITH D-MANNOSAMINE

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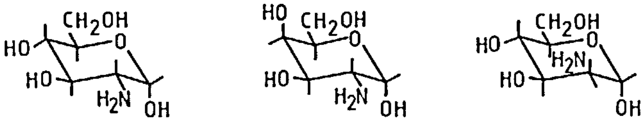
D.c. polarography was used to establish the coordination equilibria and the stability constants of the species formed at the lower pH range in solutions containing Cu(II), Ni(II) and Co(II) ions and *D*-mannosamine. Two complexes, ML and ML_2, were shown to be present for all three metal ions. The major binding site was shown to be the amino nitrogen donor. The involvement of the protonated hydroxyl oxygen of the aminosugar ligand leads to different stability constants for the complexes with particular aminosugar ligands (*e.g.*, with *D*-mannosamine, *D*-galactosamine and *D*-glucosamine). The polarographic technique was shown to be able to detect minor complexes not seen in potentiometric titrations. It effectively completes potentiometric and spectroscopic studies performed on the systems discussed in this work.

Keywords: Aminosugars, *D*-mannosamine, first-row complexes, polarography stability constants

INTRODUCTION

Recent potentiometric and spectroscopic studies on the coordination of *D*-mannosamine (ManN)[1], have shown that this amino sugar is a more effective ligand than *D*-glucosamine (GlcN) or *D*-galactosamine (GalN).[2–5] All these monomeric amino sugars act as bidentate ligands with the amino group as the main donor towards metal ions such as Cu(II), Ni(II) and Co(II). The second donor centre derives from one of the aminosugar hydroxyl groups. In the case of GlcN and GalN it appears to be HO-1 which bonds to the metal ion. The results obtained for the derivatives with this hydroxyl group blocked as in methyl-2-amino-2-deoxy-β-D-glucopyranoside[6] indicate however that other hydroxyl groups may be easily involved in metal ion coordination.

Mannosamine is an analogue of GlcN and GalN which differs only in the position of the substituents on the C-2 and/or C-4 atoms (Scheme 1). It is evident from this scheme that both the OH-1 and OH-3 groups can be considered as sterically more favourable to form chelate rings with a metal ion coordinated to the mannosamine amino group.



GlcN GalN ManN

Scheme 1

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A potentiometric study[1] indicated that ManN may form several complexes with Cu(II) and Ni(II) ions and only one species with Co(II) (Table I). In these complexes two ligand molecules are bound to the metal ion *via* amino group nitrogen atoms only in the species ML_2 or by nitrogen and deprotonated hydroxyl oxygen atoms in the (12–2) species (ML_2H_{-2}). The low concentrations of the equimolar complexes for Cu(II) and Ni(II) ions and ML and ML_2 species for Co(II) ions have not allowed the stability of these complexes to be established by potentiometric titrations. Our earlier work[3,4] has clearly shown that polarographic techniques supplement the potentiometric data calculations in such systems and are also able to describe species with very low concentrations. To complete the description of the metal ion complexes with ManN ligand we have performed the d.c. polarographic study reported below and the results are collected in this communication.

TABLE I

Values of the overall stability constants (log β) for aminosugar complexes obtained by potentiometric and polarographic methods at ionic strength 0.15 M at 25°C.

		log β					
		Potentiometry[1–3,5]			Polarography[3,4]		
Cation	Ligand	(LH)	(ML)	(ML_2)	(ML)	(ML_2)	log(K_1/K_2)
H^+	GlcN	7.700					
	GalN	7.837					
	ManN	7.689					
Cu(II)	GlcN		3.06[a]	8.76[a] 9.02	5.12	8.85	1.39
	GalN		4.20	9.13	5.23	9.02	1.44
	ManN			9.68	7.00	10.43	3.57
Ni(II)	GlcN			6.43[a] 6.73	2.95	5.62	0.28
	GalN		3.16	5.96	2.70	5.05	0.35
	ManN			6.11	3.20	5.85	0.55
Co(II)	GlcN			4.09[a]	2.30	4.95	−0.35
	GalN			6.50	2.60	5.85	−0.65
	ManN				2.50	5.70	−0.70

[a] The potentiometric data for the metal/glucosamine systems were calculated by the FICS program;[2,3] all other potentiometric data were treated with the SUPERQUAD program.[1,3,5]

EXPERIMENTAL

D-Mannosamine was used as obtained from Sigma.

A Radelkis OH 105 polarograph (Budapest) was used with a dropping mercury electrode. The saturated calomel reference electrode was connected to the polarographic cell *via* a salt bridge filled with saturated sodium perchlorate. All measurements were performed at 25°C in a medium of constant ionic strength ($0.15\,\mathrm{mol\,dm^{-3}}$ sodium perchlorate). The pH was adjusted with NaOH or $HClO_4$ solutions. The experiments were carried out under an argon atmosphere. The concentration of metal ions was $0.0001\,\mathrm{mol\,dm^{-3}}$ and the concentrations of ligand varied from 0.0001 to $0.03\,\mathrm{mol\,dm^{-3}}$.

RESULTS AND DISCUSSION

Cu(II)-ManN solutions

The electrochemical behaviour of Cu(II) ions in the presence of ManN is simple and similar to that found earlier for the other amino sugars.[3,4] The two-electron reduction waves of Cu(II) over the pH range studied are reversible and diffusion-controlled. They are shifted to more negative potentials as the pH increases. Detailed examination of the polarograms obtained showed the presence of the two species CuL and CuL_2. The stability constants evaluated by the DeFord-Hume approach[7] for both complexes are given in Table I. For comparison, the stabilities of the GalN and GlcN complexes are also collected in Table I. The polarographic results indicated very clearly the presence of the equimolar complex also in the case of the ManN ligand. The stability constants for the CuL species obtained from the polarographic data indicate that the stability of the Cu(II)ManN complex is considerably higher than those evaluated for the other two aminosugar ligands as shown in Table I. As was concluded earlier,[1-6] the main binding site of the ligand molecule is the amino group. Considering the fact that the pK values of this group for all three ligands are very close to each other, the differences in the stability constants indicate that besides nitrogen coordination, the protonated hydroxyl donor is also involved in metal binding.[2] The same argument may also explain the fact that the CuL_2 complex with ManN is the strongest among the three amino sugars discussed. The data presented in Table I show that the stability constant for the latter complex evaluated from polarographic data is distinctly different from that obtained from potentiometric titrations. One of the reasons for this difference is the fact that calculations based on potentiometric titrations do not include the equimolar complex because of its low concentration.

TABLE II

Values of the limiting currents (i), average ligand numbers (p) and dissociation rate constants (k_b) for different ligand concentrations in Ni(II)/*D*-mannosamine solution at pH 7.68 M $NaClO_4$[a].

c_{tot}(mol dm^{-3})	i_k (uA)	i_d (uA)	i_d^M (uA)	p	k_b (s^{-1})
0.0000			0.7272		
0.0001	0.0576	0.7272	0.6696	1	0.2966
0.0002	0.1116	0.7236	0.6120	1	0.3419
0.0004	0.1980	0.7200	0.5220	1	0.3718
0.0007	0.2880	0.7056	0.4176	1	0.3886
0.0010	0.3528	0.6948	0.3420	1	0.4359
0.0020	0.4680	0.6696	0.2016	1	0.5544
0.0040	0.5436	0.6372	0.0936	2	0.9128
0.0070	0.5796	0.6120	0.0324	2	0.8660
0.0100	0.5832	0.5976	0.0144	2	1.1150
0.0200	0.5832	0.5832	0.0000		
0.0300	0.5832	0.5832	0.0000		

[a] Ni(II) = 0.0001 mol.dm^{-3}; drop time 4.1 s; c_{tot} corresponds to total ligand concentration; i_k, limiting current of the complex reduction wave; i_d, total limiting current; i_d^M, limiting current of the nickel aquo ion; k_b was calculated.[4]

Ni(II)-ManN solutions

Ni(II) aqua ions in the electrolite used are characterized by a well shaped, two-electron, irreversible reduction wave at about −1.0 V. In the presence of ManN the metal ion reduction follows the pattern observed for the other aminosugars.[4] In the pH range 5.5–8 two reduction waves are observed (Fig. 1). The wave at −0.81 V which increases with pH corresponds to the reduction of the nickel complex with ManN while the other one at −1.0 V may be attributed to the reduction of uncoordinated metal ions. At a pH slightly above 8 only one reduction wave for complexed metal is present and it moves to more negative potentials when pH is increased further. In order to establish the nature of the complexes formed the measurements were made at pH 7.68. The metal ion concentration was constant while aminosugar concentration varied from 0.0001 to 0.03 mol dm^{-3}. The results are collected in Table II. The reduction wave of the complex species is kinetically-controlled and for further analysis the Koutecký equation for limiting current was used.[8,9] The details of this approach are given in our earlier work.[4] The results of the calculations indicate that two complexes are present in the solutions studied, NiL and NiL_2, and that the latter species is the complex which undergoes reduction at −0.81 V. The stability constants were calculated from the variations of the limiting current and are given in Table II. Again, the use of the polarographic technique indicates the formation of the equimolar complex with a stability higher than for the other two ligands, though to lesser extent than in the case of the Cu(II) complexes (Table I). The stability of the NiL_2 complex is close to that evaluated from potentiometric data.

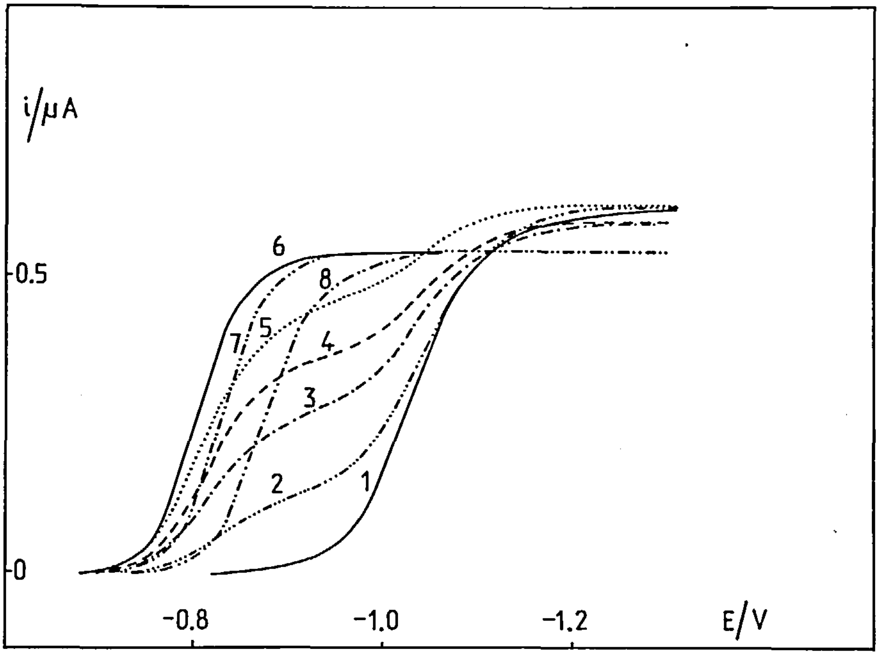

FIGURE 1 D.c. polarograms of the Ni(II)/*D*-mannosamine solutions at different pH (drop time 4.1 s). [Ni(II)] = 0.0001 mol dm^{-3}; [ManN] = 0.01 mol dm^{-3} in 0.15 M $NaClO_4$; pH: (1) 4.32; (2) 6.18; (3) 6.58; (4) 6.84; (5) 7.08; (6) 7.83; (7) 8.64; (8) 9.38.

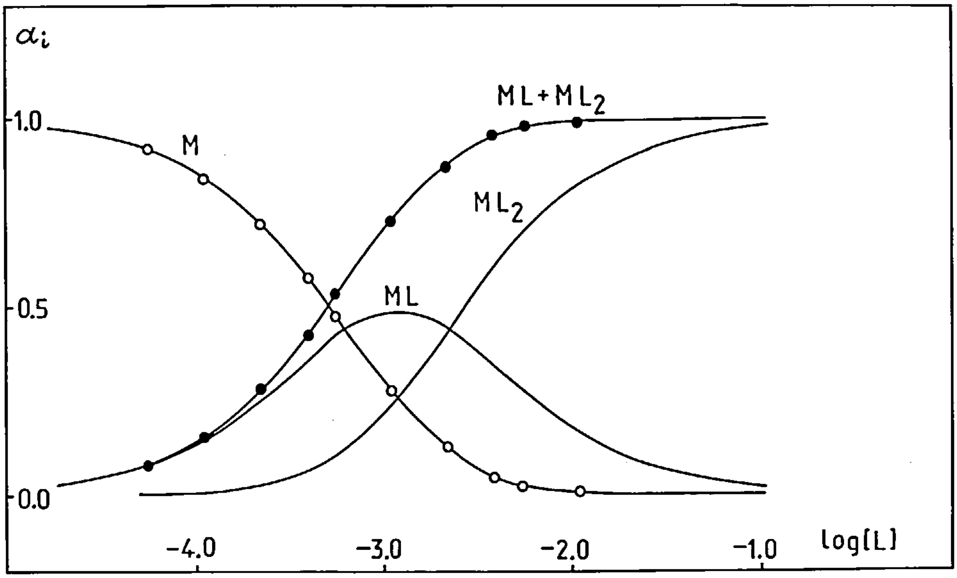

FIGURE 2 The distribution of species as a function of log[L] in solutions containing Ni(II) and *D*-mannosamine; experimental points are calculated from the ratios of the respective limiting currents.

The results obtained indicate the scheme of polarographic reduction of Ni(II) ions in the aqueous solutions of ManN as follows,

$$\begin{array}{lcl} \mathrm{Ni(II)_{aq}}^{2+} \rightleftharpoons \mathrm{NiL}^{2+} & \underset{k_b}{\overset{k_f}{\rightleftharpoons}} & \mathrm{NiL_2}^{2+} \\ \Big\downarrow \quad \alpha_o = 0.41,\ (-1.0\,\mathrm{V}) & & \Big\downarrow \quad \alpha_2 = 0.58, \quad (-0.81\,\mathrm{V}) \\ \mathrm{Ni_{(Hg)}} & & \mathrm{Ni_{(Hg)}} \end{array}$$

where $k_b = 0.96\,s^{-1}$.

Co(II)-ManN solutions

The reduction waves of Co(II) ions in the presence of ManN at different pH are shown in Fig. 3. The reduction wave is diffusion-controlled and it is shifted towards less negative potentials as pH increases up to 8. At higher pH it moves to more negative potentials and its limiting current decreases slightly. The positive shift of the reduction wave in the presence of ligand indicates that the species formed at pH below 8 undergo easier reduction than the Co(II) aqua ion. In order to establish the composition of the complexes formed and their stability constants, the measurements were performed at constant pH (7.95) for solutions containing a constant concentration of metal ions and variable concentrations of ligand from 0.0001 to $0.016\,\mathrm{mol\,dm^{-3}}$. The anlaysis of the obtained reduction waves was carried out according to the approaches proposed by Ruzić,[10-11] Matsuda and Ayabe[12] and Biernat.[13] The results of this analysis indicate that, at low concentrations of ligand, the reduction of Co(II) aqua ions is the dominant process on the mercury electrode

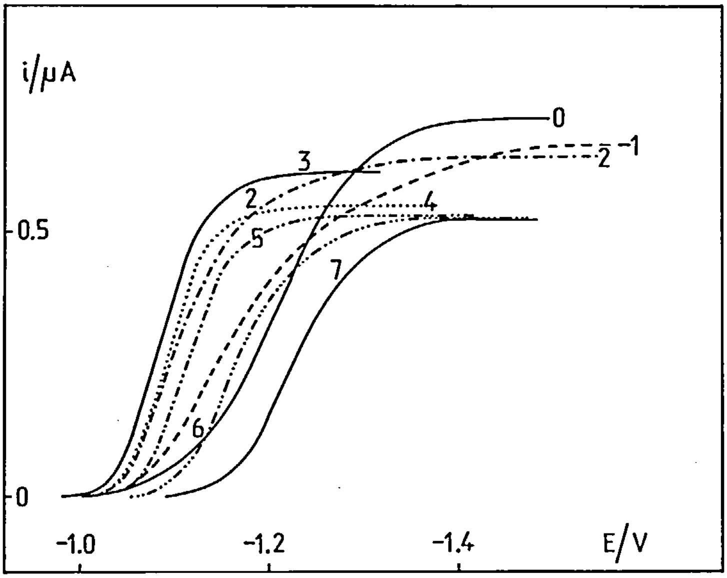

FIGURE 3 D.c. polarograms for Co(II)/*D*-mannosamine solutions at different pH (drop time 4.72 s) with 0.0001 mol dm^{-3} Co(II) and 0.01 mol dm^{-3} ManN in 0.15 M $NaClO_4$; pH: (1) 6.40; (2) 6.94; (3) 7.86; (4) 8.27; (5) 8.65; (6) 9.42; (7) 10.31.

while at higher concentrations the dominant species undergoing reduction is the CoL_2^{2+} complex.[4] The half-wave potential shifts of the cobalt species reduced at the electrode as a function of the ligand concentration are shown in Fig. 4. Using the equations given by Biernat[13] for the irreversible reduction waves, the rate of the electrode reactions and the stability constants of CoL^{2+} and CoL_2^{2+} were evaluated. The rates of the electrode reactions for both reducible species at potential −1.213 V were found to be $k^\circ_0(Co(II)_{aq})^{2+} = 1.568 \times 10^{-3}\,cm\,s^{-1}$ and $k^\circ_2(CoL_2)^{2+} = 1.725\,cm\,s^{-1}$ for the reaction scheme shown below.

$$\begin{array}{lll} Co(II)_{aq}{}^{2+} \rightleftharpoons & CoL^{2+} \rightleftharpoons & CoL_2{}^{2+} \\ \downarrow \quad \alpha_0 = 0.32,\ k^\circ_0 & & \downarrow \quad \alpha_2 = 0.686,\ k^\circ_2 \\ Co_{(Hg)} & & Co_{(Hg)} \end{array}$$

The stability constants (Table I) for both complexes CoL and CoL_2 are close to those found for the respective species with GalN and slightly higher (especially for CoL_2) that those of GlcN complexes.

The data presented above clearly indicate that polarographic measurements are able to effectively complete the potentiometric study. The stability constants for the species which are not revealed by the potentiometric data calculations can be evaluated quite precisely. Since the concentrations of the ML species are often very low, the potentiometric evaluation of its stability is rather inaccurate. A good example of such calculations is given in Table I for Cu(II)-GlcN and GalN systems. In both cases the log K_1 stability constants for the CuL species obtained from the potentiometric data are distinctly lower than the log K_2 value (*i.e.*, log $(K_1/K_2) < 0$).

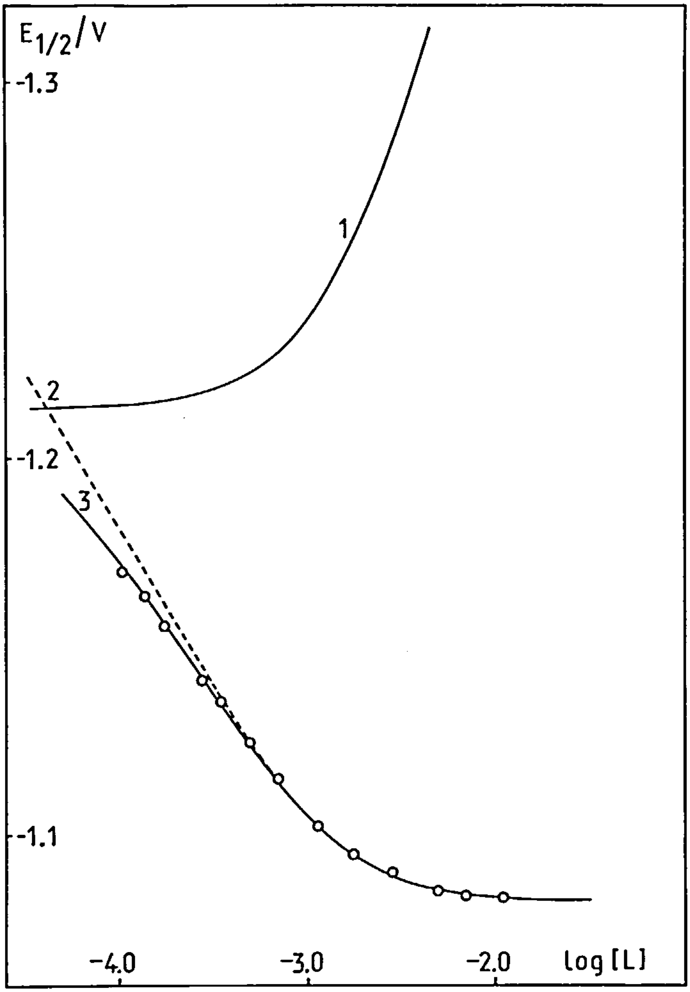

FIGURE 4 The possible changes of the half-wave potentials, assuming that the reduction of Co(II)/*D*-mannosamine complexes proceeds by the Co(II) aquo ion only (1), the CoL_2 complex only (2), or the total reduction of both these forms (3); (o): experimental points.

Since there are no major interligand interactions or changes of metal ion symmetry, any explanation of this result needs to assume that the estimation of log K_1 value is incorrect due to the very low concentration of the ML complex. The respective values obtained from the polarogaphic data (Table I) are much more realistic. The log (K_1/K_2) ratio obtained from the polarographic data varies for particular metal ion complexes (Table I). This result suggest some slight differences in the position of the bound ligand molecules in particular cases, although, error deriving from the approximation used can not be excluded.

The results obtained indicate that at lower pH regions aminosugars form two monodentate species with Cu(II), Ni(II) and Co(II) ions, ML and ML_2. The main coordination site in these complexes is an amino nitrogen donor. The involvement of the protonated hydroxyl oxygen is however also evident. Interaction with the latter donor leads to different stability constants for the complexes with particular aminosugar ligands.

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REFERENCES

1. H. Kozlowski, P. Decock, I. Olivier, G. Micera, A. Pusino and L.D. Pettit, *Carbohydr. Res.*, in press.
2. G. Micera, S. Deiana, A. Dessi, P. Decock, B. Dubois and H. Kozlowski, *Inorg. Chim. Acta*, **107**, 45 (1985).
3. J. Lerivrey, B. Dubois, P. Decock, G. Micerak, J. Urbańska and H. Kozlowski, *Inorg. Chim. Acta*, **125**, 187 (1986).
4. J. Urbańska, H. Kozlowski, A. Delannoy and J. Hennion, *Anal. Chim. Acta*, **207**, 85 (1988).
5. B. Radomska, H. Kozlowski, P. Decock, B. Dubois and G. Micera, *J. Inorg. Biochem.*, **33**, 153 (1988).
6. A. Pusino, D. Droma, P. Decock, B. Dubois and H. Kozlowski, *Inorg. Chim. Acta*, **138**, 5 (1987).
7. D. D. De Ford and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
8. J. Koutecký. *Chem. Listy*, **47**, 323 (1953).
9. Z. Galus, in "Procesy Elekrodowe Ni(II) na Elektrodach Rteciowych" (PWN, Warszawa, 1966).
10. I. Ruzić and M. Branica, *J. Electroanal. Chem.*, **22**, 243 and 422 (1969).
11. I. Ruzić, *J. Electroanal. Chem.*, **29**, 440 (1971).
12. H. Matsuda and Y. Ayabe, *Bull. Chem. Soc. Jpn.*, **29**, 134 (1956).
13. J. Biernat and M. Baranowska-Zralko, *Electrochim. Acta*, **17**, 1867, (1972).