# Formation of D-Glucosamine Complexes with Cu(II), Ni(II) and Co(II) Ions

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## Abstract

The potentiometric and spectroscopic results for Cu(II), Ni(II) and Co(II) ion complexes with D-glucosamine and the polarographic results for Cu(II)–D-glucosamine systems are discussed. Cu(II) and Ni(II) form two major complex species, *i.e.*: $ML_2$ and $ML_2H_{-2}$. Co(II) forms only the latter complex in which two D-glucosamine molecules are chelating to metal ion via $\{NH_2, O^-\}$ donor sets.

The values of stability constants obtained by two different programs (F.I.C.S. and SUPERQUAD) as well as those calculated from polarography for Cu(II) complexes are similar for the major species. The correlation of the potentiometric results with those obtained from spectroscopy and polarography seems to be necessary for reasonable description of the systems studied.

## Introduction

Our recent work on Cu(II) complexes with D-glucosamine has shown that the aminosugar is a very efficient ligand forming stable chelates with metal ion [1].

Since sugars and aminosugars as well as their polymer derivatives (e.g. chitosan, chitine or pectin) are naturally occurring and effective ligands [2–4], we have undertaken a detailed study on sugar and aminosugar complexation ability with different essential and toxic elements. Some results are presented in this communication.

## Experimental

Potentiometric studies were performed using modified analytical potentiometry (F.I.C.S.) adapted to the Apple II computer [1] and with a SUPERQUAD program [5] adapted to the IBM-PC microcomputer equipped with a 8087 coprocessor. The F.I.C.S. program used (Free Ionisation Concentration of Species) is a modified version of the earlier programs published by Sarker [6] and Laurie [7]. The critical survey of this approach was presented by Guevremont and Rabenstein [8].

The version of F.I.C.S. used, as well as the microcomputer adaptation of SUPERQUAD, were checked on Ni(II)–glycine system and the results obtained are very close to those published in the literature [5]. The microcomputer version was found to give the same log values as the original SUPERQUAD version for Ni(II)–triaminotripropylamine, Ni(II)–D-Histidine-L-Proline as well as Ni(II)–glycine systems (the same input data contributed to give the same output).

The potentiometric titrations were carried out on a Tacussel ISIS 20000 pH-meter at 25 ± 0.03 °C with a TB 10/HA glass electrode and a KCl saturated reference electrode. The solutions were prepared in deionized and bidistilled water under argon atmosphere. D-glucosamine was used as obtained from Sigma. The stock solutions of ligand were prepared in 0.15 M NaCl. The concentrations of ligands and protons introduced in potentiometric cell were verified by SUPERQUAD and $pK_a$ SIMPLEX [6] programs. Carbonate-free 0.1013 M NaOH was prepared in 0.15 M NaCl and standardized against phthalate (National Bureau of Standards). Puratronic cupric, nickel and cobalt chlorides were used to prepare respective metal ion solutions checked by titration with EDTA. The quantity, in micromoles, of metal and D-glucosamine used in titrate are given in Table I.

Absorption spectra were recorded on a Beckman Acta 7 spectrophotometer and CD spectra on a Jobin Yvon Mark III spectropolarimeter for the solution with metal concentration $5 \times 10^{-3}$ M and 5 or 10-

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TABLE I. Quantity of Metal and D-Glucosamine Used in Titrations (μmol)

| Cu | D-glucosamine | Ni | D-glucosamine | Co | D-glucosamine |
|---|---|---|---|---|---|
| 2 | 28.75 | 2.24 | 45 | 1.05 | 45 |
| 3 |  | 4.475 |  | 2.1 |  |
| 4 |  | 8.95 |  | 4.2 |  |
| 3 | 15.8 | 4.475 | 30 | 2.1 | 30.375 |
|  | 28.75 |  | 45 |  | 45 |
|  | 40.7 |  | 60 |  | 60.75 |

TABLE II. Logarithms of Stability Constants log $\beta_{pqr}$ of Complex Species in 0.15 M NaCl at 25 °C

| $M_pL_qH_r$ Species |  |  | log $\beta_{pqr}$ |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| $p$ | $q$ | $r$ | Cu |  |  | Ni |  | Co |  |
|  |  |  | F.I.C.S. | SUPERQUAD | Polarography[a] | F.I.C.S. | SUPERQUAD | F.I.C.S. | SUPERQUAD |
| 1 | 1 | 0 | 3.06 |  | 5.12 |  |  |  |  |
| 1 | 2 | 0 | 8.76 | 9.02 (0.026) | 8.85 | 6.43 | 6.73 (0.05) | 4.09 |  |
| 1 | 2 | −1 | 0.83 |  |  | −3.03 |  | −3.89 |  |
| 1 | 2 | −2 | −5.82 | −5.26 (0.03) |  | −12.13 | −11.58 (0.07) | −13.08 | −12.20 (0.03) |
| 1 | 2 | −3 | −15.08 | −13.77 (0.05) |  |  |  |  |  |
|  |  |  |  | $\chi^2 = 4.11$<br>$\sigma = 4.07$ |  |  | $\chi^2 = 2.17$<br>$\sigma = 4.17$ |  | $\chi^2 = 11.51$<br>$\sigma = 2.27$ |

[a] The stability constants were obtained with the procedure originally proposed by Lingane [18].

fold excess of ligand. The $\Delta\epsilon$ values ($\epsilon_L - \epsilon_R$) were calculated for the total concentration of metal ions in the solution.

Polarographic measurements were carried out on a Radelkis OH-105 polarograph at 25 °C under argon in 0.15 M $NaClO_4$.

## Results and Discussion

Cu(II)–D-glucosamine results have been presented in previous work [1]. In this work we have recalculated the potentiometric data using the SUPERQUAD program [5]. The stability constants obtained by F.I.C.S. and SUPERQUAD programs as well as those from polarography are given in Table II.

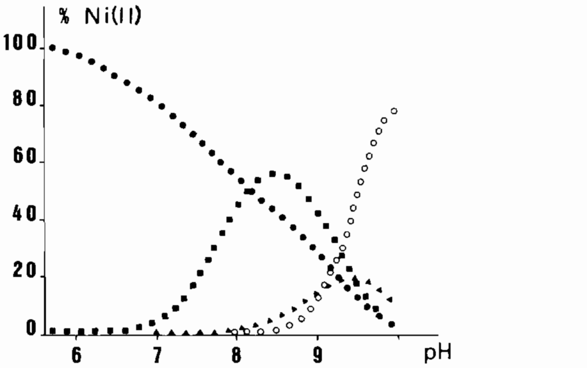


Fig. 1. Species distribution in the Ni(II)–D-glucosamine system in function of pH: 100 (●), 120 (■), 12-1 (▲), 12-2 (○).

### *Ni(II)–D-Glucosamine System*

The stability constants obtained from the F.I.C.S. and SUPERQUAD programs are given in Table II. Both programs described reasonably well two major species present in the solution, *i.e.* $NiL_2$, (120), and $NiL_2H_{-2}$, (12-2). The $NiL_2H_{-1}$, (12-1), complex seen by F.I.C.S. calculation as a minor species (Fig. 1) is rejected by SUPERQUAD. The absorption spectra shows that in the entire studied pH range of 3–10.5 the nickel complexes are always octahedral. The three d–d transitions observed for $NiL_2$ (pH 8.2) at 1048 ($\epsilon = 4.5$ $M^{-1}$ $cm^{-1}$), 637 ($\epsilon = 5$ $M^{-1}$ $cm^{-1}$) and 380 nm ($\epsilon = 11$ $M^{-1}$ $cm^{-1}$) and $NiL_2H_{-2}$ (pH 10.5) at 1040 (7), 625 (8) and 380 nm (18) correspond well to the two nitrogen-bound octahedral complexes [10, 11].

The coordination of D-glucosamine to nickel ions is more clearly seen in the CD spectra (Fig. 2). The coordination starts in the vicinity of pH ~ 7, giving the Cotton effects for the d–d transitions which are observed for pH 8.4 at 700 ($\Delta\epsilon = -0.01$), 440 ($\Delta\epsilon = +0.006$) and 375 nm ($\Delta\epsilon = -0.017$). This result agrees well with the formation of $NiL_2$ species (Fig. 1). This spectrum changes considerably when

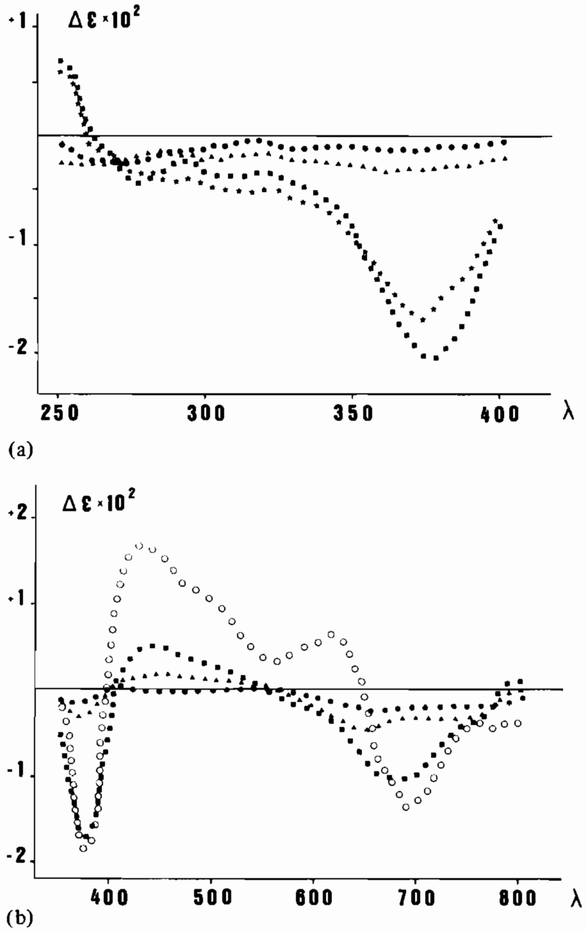


Fig. 2. Circular dichroism spectra of Ni(II)–D-glucosamine solutions in (a) the charge transfer region at pH: 5.33 (●), 7.70 (▲), 8.4 (★), 9.0 (■); and (b) the d–d region at pH: 6.67 (●), 7.70 (▲), 8.4 (■), 9.0 (○).

the pH increases to pH ~ 9 (Fig. 2). The positive Cotton effect appears at 620 nm ($\Delta\epsilon = +0.006$), and the band at 440 becomes much stronger and asymmetric (Fig. 2). The transition observed at 245 nm as a positive Cotton effect corresponds well to $NH_2 \rightarrow Ni(II)$ charge transfer transition. The corresponding transition for Cu(II) complex was observed at 300 nm. This high energy shift of charge transfer transitions of this order is usually observed for Ni(II) complexes, e.g. with peptides, when compared to corresponding Cu(II) complexes [12].

### *Co(II)–D-Glucosamine System*

The stability constants are given in Table I. The $CoL_2$, (120), and $CoL_2H_{-1}$, (12-1), species are only minor (~5%) and are not seen in the SUPERQUAD calculations (Fig. 3).

The formation of $CoL_2H_{-2}$ complex at pH > 9 is seen clearly in the CD spectra. There are three bands at 640, 560, and 460 nm (Fig. 4b) corresponding to the d–d transition and 260 and 220 nm Cotton effects which could be assigned as the charge transfer transitions. The analysis of charge transfer transitions for Cu(II), Ni(II) and Co(II) complexes made on the basis of oxidizing power [13] strongly suggests the 220 nm band as a $NH_2 \rightarrow Co(II)$ charge transfer transition. Hence, the origin of the other band is unclear. It should be mentioned here that the CD spectra recorded on a very high sensitivity scale (Fig. 4a) clearly support the formation of minor species already close to pH 7; this could support the F.I.C.S. calculation data given in Fig. 3 and Table I for two minor (120) and (12-1) complexes. The $\Delta\epsilon$ values observed for the latter species are almost two orders lower than those observed for the complex formed around pH 9–10 (Fig. 4a and b).

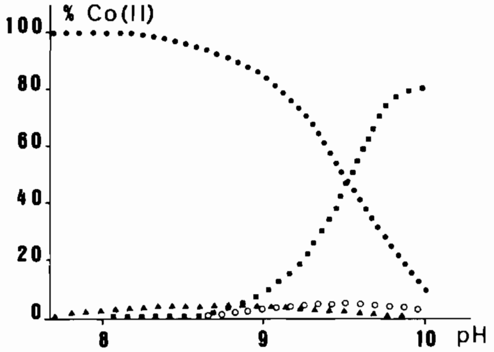
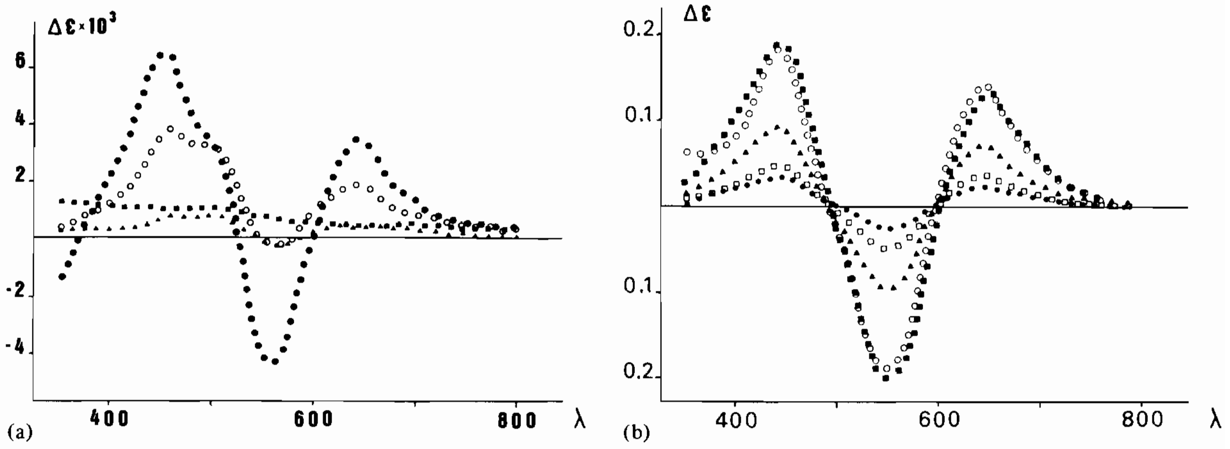


Fig. 3. Species distribution in the Co(II)–D-glucosamine system in function of pH: 100 (●), 120 (▲), 12-1 (○), 12-2 (■).

The comparison of the stability constants of Cu(II), Ni(II) and Co(II)–D-glucosamine complexes (Table II) gives normal orders of complex stability as predicted by Irving and Williams, *i.e.* Cu > Ni > Co. All three metals bind two ligand molecules with eventual formation of $MLH_{-2}$ complex in which D-glucosamine binds to the central ion via $NH_2$ and deprotonated hydroxyl group. The results obtained in this work are in general agreement with earlier works [14–16], although no 1:1 complexes proposed earlier [11, 13] could be observed in our experiment.

The F.I.C.S. and SUPERQUAD calculations differ mainly in the acceptance of the minor species which could be present in the solution. For the major complexes, the SUPERQUAD, which rejects most minor complexes, usually gives higher $\log\beta$ values (~0.5 units) than F.I.C.S.

The polarographic measurements carried out for Cu(II) complexes strongly indicate the presence of the CuL (110) complex seen as a minor species by F.I.C.S. calculations. The $\log\beta_{110}$ values obtained from polarographic results are, however, considerably higher than those calculated from potentiometric data. The comparison of the stepwise stability constant ratio $K_1/K_2$ for Cu(II)–D-glucosamine with those of, for example, Cu(II)–$NH_3$ or related systems [17] seems to suggest that the $\log\beta_{110}$ value obtained



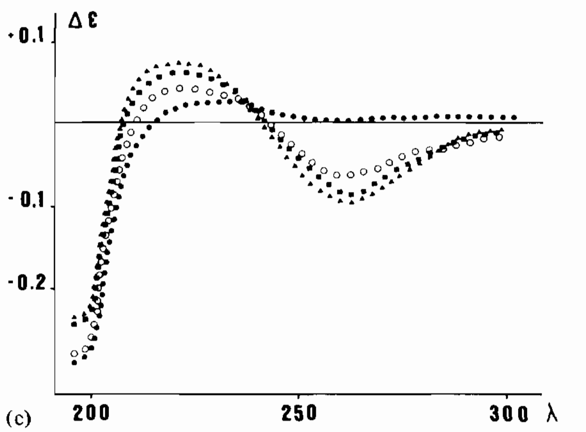


Fig. 4. Circular dichroism spectra of Co(II)–D-glucosamine solutions in (a) the d–d region at pH: 4.49 (▲), 6.33 (■), 7.0 (○), 7.68 (●); (b) the d–d region at pH: 7.75 (●), 8.24 (▲), 8.71 (○), 8.0 (□), 9.35 (■); and (c) the charge transfer region at pH: 8.1 (●), 8.9 (○), 9.3 (■), 10.4 (▲).

from polarography is more reasonable. The log $\beta_{120}$ value calculated from polarographic data corresponds reasonably well to the values obtained from the potentiometric results (Table II). The discussion presented above clearly indicates the necessity of the multitechnique approach to the study of metal ion complexation even by relatively simple ligands.

## Acknowledgement

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