Inorganica Chimica Acta, 46 (1980) 153–155
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Solution Studies of Systems with Polynuclear Complex Formation. 2. The Nickel(II) Citrate System

EBBE R. STILL* and PETER WIKBERG

Department of Chemistry, Åbo Akademi, SF-20500 Åbo 50, Finland

Received December 12, 1979

Complex formation between nickel and citrate ion (citric acid = H_3L) has been investigated on account of the reported hyperaccumulation of nickel by some primitive plants. Evidence is given for the formation of a polynuclear complex species of the composition $Ni_4(OH)_4L_3^{5-}$ or $Ni_4OH(H_{-1}L)_3^{5-}$ in weakly alkaline solutions. The result is in agreement with a crystallographic study. The stabilities of the polynuclear complex and of the mononuclear species NiL_2^{4-} and NiHL were determined.

Introduction

The uptake and translocation of cations by plants is a problem of considerable interest. It has been demonstrated [1] that plants respond to excess levels of cations by an increased synthesis of organic acids, and that the transport of cations in the xylem fluid is facilitated by the formation of metal chelates of moderate stability. The ligands in question may be ether-extractable organic acids or specific hydroxycarboxylic acids such as malic and citric acid.

The role of citric acid in cell physiology relates mostly to cellular metabolism. Released from metabolic sites and moving in the xylem fluids the anion will have chelating properties masking the hydrolysis of most transition metal cations.

It has been shown that iron uptake by plant roots and transport to the xylem involves complex formation with citrate ion [2]. It has also been suggested that the hyperaccumulation of nickel (0.1–5% Ni of dry mass) by some primitive angiosperms is due to nickel citrate complexes [3]. This extraordinary property is mainly shown by species of the order Violales (*Flacourtiaceae* and *Violaceae*) growing on ultrabasic rocks in New Caledonia.

The aim of the present paper is to reinvestigate the nickel citrate system. The investigation was carried out to elucidate the composition and stability of the nickel complexes formed in weakly alkaline solutions, where a deprotonation of the alcoholic group of the ligand may take place.

Bobtelsky *et al.* have investigated several metal citrate and tartrate systems. In the nickel citrate system [4] they found evidence of hydrolysis reactions to occur leading to complex species with an OH/Ni ratio of 1:1 and 2:1, respectively. A more recent equilibrium study has revealed the presence of polynuclear species in solution [5]. The experimental points in the early part of the buffer region were explained by introduction of the dimeric complex $Ni_2(H_{-1}L)_2$, but it was admitted that other hydroxy species may be present in solution as well.

A crystallographic study of the nickel complex of quadruply ionized citrate ion has been reported by Strouse *et al.* [6]. The crystal structure can be described as two clusters of $Ni_4OH(H_{-1}L)_3^{5-}$ containing the ligand in its quadruply ionized form and a triply bridging hydroxide ion. The two clusters are joined together through bridging citrate carboxyl groups. J. Strouse [7] also reported the results obtained from solution studies of Fe(II) and Ni(II) citrate complexes. It was assumed that the two nickel citrate clusters are separated in solution and that the triply bridging hydroxide ion is replaced by a quadruply ionized citrate ion resulting in a tetrameric complex of 4:4 nickel:citrate stoichiometry.

Experimental

The investigation was carried out at 25 ± 0.1 °C in solutions of ionic strength 0.1 mol/l (KNO_3). All chemicals were of reagent grade, and were used as received. The experimental setup was as described in our previous paper [8], where the protonation constants of the ligand were also given.

Results

Most of the stability constants given in the literature [9] are reported for 1:1 chelates of the type

---

*On leave at Inorganic Chemistry Laboratory, University of Oxford, Oxford, U.K.

NiHL and NiL$^-$. A representative value for the complex NiL$^-$ is log $K_{NiL}^{Ni,L}$ = 5.30 (25 °C, 0.1 mol/l KNO_3) [5, 9]. The formation of a NiL_2^{4-} complex is probable. The situation was clarified by a potentiostatic titration at pH 7.0 (urotropin buffer) in Fig. 1. The formation of a weak NiL_2^{4-} complex was observed: log $K_{NiL_2}^{L,NiL}$ = 2.85 ± 0.02. The calculations were based on standard graphical and numerical methods (see, *e.g.*, [10]) and the complex formation between sodium and citrate ions (log $K_{NaL}^{Na,L}$ = 0.7 [9]) was taken into account. The stability of the NiHL complex was evaluated from a photometric titration where the pH of the solution was varied by the addition of a nitric acid solution. The result log $K_{NiHL}^{Ni,H,L}$ = 8.75 ± 0.01 is in agreement with previously reported data [5, 9].

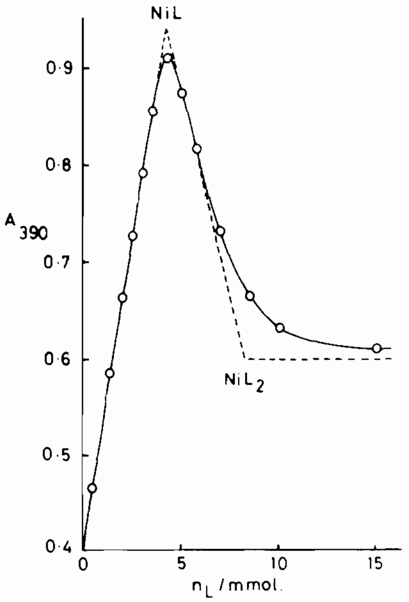

Fig. 1. The absorbance at 390 nm of 50 ml of a solution containing 4.2 mmol of a Ni(II) salt as a function of added amount of citrate. The pH of the solution was kept constant at a value of 7.0.

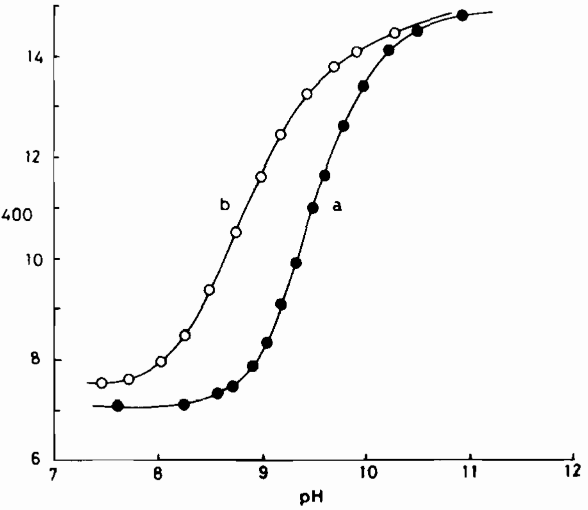

Fig. 2. The molar absorbtivity at 400 nm as a function of pH. Curve a. C_{Ni} = 0.022 mol/l, C_L = 0.067 mol/l. Curve b. C_{Ni} = 0.036 mol/l, C_L = 0.054 mol/l. (C denotes total concentration).

The complex formation of the nickel(II) complex with quadruply ionized citrate ion is demonstrated in Fig. 2. The figure shows that the complex is fully formed at a pH value of 10 or 10.5. An investigation of the composition of the complex formed can be carried out as a potentiostatic titration. The results obtained in titrations at pH 10.0 and 10.5, respectively, are plotted in Fig. 3. The pH-value of the solution is maintained at a constant value by addition of standardized NaOH solution and the consumption of base is plotted as the ordinate in the figure. The absorbance of the solution at 400 nm was also measured during the titration and the results from the titration at pH 10 are displayed in Fig. 3.

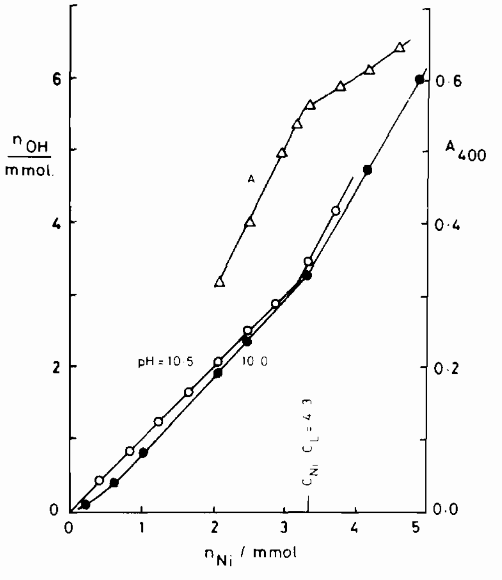

Fig. 3. Potentiostatic titration at pH 10.0 and 10.5 of 2.5 mmol of citrate ion in 100 ml solution. The amount of base consumed (in mmol) and the absorbance at 400 nm (pH 10) are plotted as a function of the amount of nickel ion added to the solution.

Figure 3 shows that 1 mol of OH$^-$ is consumed per mole of nickel added. The break in the base consumption and in the absorbance curves occur at a 4:3 nickel:citrate ratio. The result can be interpreted in terms of a $Ni_4(OH)(H_{-1}L)_3^{5-}$ complex in solution. The choice of a tetrameric complex, rather than a multiple thereof, is based on the molecular weight determinations reported by Strouse [7]. The data for the depression of the sodium sulphate transition temperature indicated tetramer formation in solution, whereas the freezing point depression results obtained in solutions of low ionic strength were interpreted by Strouse [7] in terms of dimeric species. The latter data are, however, equally well explained in terms of a tetrameric nickel citrate complex of 4:3 nickel: citrate stoichiometry and the excess of ligand as free citrate in solution.

The equilibrium constant for the reaction

$$4NiL^{-}\ (+H_2O) \rightleftharpoons Ni_4OH(H_{-1}L)_3^{5-} + L^{3-} + 4H^{+} \qquad K_{tetramer}$$

was evaluated from the absorbance curves of Fig. 2: $\log K_{tetramer} = -28.3 \pm 0.1$ or $\log K(4Ni^{2+} + 3L^{3-} \rightleftharpoons Ni_4OH(H_{-1}L)_3^{5-} + 4H^{+}) = -7.1$.

Discussion

It is well known that the formation of polynuclear hydrolysis products of metal ions is due to the rather strong tendency of OH^- to coordinate more than one cation in solution and to form hydroxide bridges. The crystal structure of the nickel citrate complex [6] shows that the ionized hydroxyl group of the ligand exhibits doubly and triply bridging configurations. We may consider the citrate ligand as a substituted water molecule, and it follows that the composition of the metal complexes of quadruply ionized citrate may be compared to the corresponding polynuclear hydrolysis products. Steric and electrostatic factors have to be taken into account.

The principal polynuclear hydrolysis product of Ni^{2+} is the tetramer [11], $Ni_4(OH)_4^{4+}$, which can be compared to the $Ni_4OH(H_{-1}L)_3^{5-}$ complex investigated above. The main hydrolysis product of Cu^{2+} is $Cu_2(OH)_2^{2+}$ and the analogy with the citrate complex $Cu_2(H_{-1}L)_2^{4-}$ is striking. In the case of ferric iron a dimer $Fe_2(OH)_2^{4+}$ is the dominating hydrolysis product in solutions of moderate Fe^{3+} concentrations. The formation of a dimeric citrate complex $Fe_2(H_{-1}L)_2^{2-}$ has been reported [9]. J. Strouse reported [7] the formation of a tetrameric iron(II) citrate complex. However, polynuclear hydrolysis products of Fe(II) have not been reported due to early hydroxide precipitation [11].

Polynuclear complex formation in solutions of moderate concentrations (total concentrations in the mmol/l range and an excess of the ligand) starts at low pH values in the copper(II) citrate system, but at considerably higher pH values (pH > 8) in the analogous nickel(II) system. This implies that polynuclear complex formation may not be the uptake mechanism of nickel accumulating plants and a mechanism based on ternary nickel–citrate–amino acid complexes seems more probable.

Acknowledgements

Preliminary results of our work were presented by E.S. at *Coordination Chemistry in Solution* Conference, Lund, Sweden, in June 1977. The authors are greatly indebted to Dr. Francis J. C. Rossotti for his pertinent remarks on the manuscripts and to Prof. Robert J. P. Williams for valuable discussions. For financial support we thank the Academy of Finland and The Royal Society, London, for a fellowship in the European Science Exchange Program for E. Still and the Åbo Akademi Foundation for grants to P. Wikberg.

References

1 K. K. Torii and G. G. Laties, *Plant Cell Physiol., 7,* 395 (1966).
2 L. O. Tiffin, in 'Micronutrients in Agriculture', Eds. J. J. Mortvedt, P. M. Giordano and W. L. Lindsay, pp. 199–229, Soil Sci. Soc. Am., Madison, Wisc. (1972).
3 T. Jaffré, W. Kersten, R. R. Brooks and R. D. Reeves, *Proc. R. Soc. Lond. B, 205,* 385 (1979).
4 M. Bobtelsky and J. Jordan, *J. Am. Chem. Soc., 67,* 1824 (1945).
5 P. G. Daniele and G. Ostacoli, *Ann. Chim. (Rome), 66,* 537 (1976).
6 J. Strouse, S. W. Layten and C. E. Strouse, *J. Am. Chem. Soc., 99,* 562 (1977).
7 J. Strouse, *J. Am. Chem. Soc., 99,* 572 (1977).
8 E. R. Still and P. Wikberg, *Inorg. Chim. Acta, 46,* 147 (1980)
9 L. G. Sillén and A. E. Martell, 'Stability Constants of Metal Ion Complexes', Special Publication Nos. 17 and 25, The Chemical Society, London (1964 and 1972).
10 R. W. Ramette, *J. Chem. Educ., 11,* 647 (1967).
11 C. F. Baes, Jr. and R. E. Mesmer, 'The Hydrolysis of Cations', Wiley–Interscience, New York (1976).