

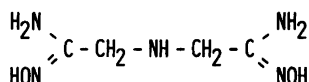
The Complex Formation of Copper(II) and Nickel(II) with Iminobis(acetamidoxime)

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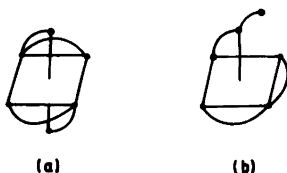
The protonation and complex formation equilibria of iminobis(acetamidoxime), L, with copper(II) and nickel(II) ions have been studied in aqueous 1.0 M (Na)ClO₄ solution at 25 °C by potentiometric titrations with the use of a glass electrode. The emf data may be explained by assuming three protonation equilibria, giving rise to the species HL⁺, H₂L²⁺ and H₃L³⁺, and by formation of the stepwise complex ions ML²⁺ and ML₂²⁺ as well as the deprotonated species H₋₁ML₂⁺ (M=Cu²⁺ or Ni²⁺). The relevant equilibrium constants were evaluated by using the least-squares computer program MINQUAD.

Complex formation of 2-aminoacetamidoxime and its *N*-methylated derivatives with nickel(II) and copper(II) ions has been described in earlier publications from this laboratory.^{1,2} With these bidentate ligands the different *N*-substitutions lead to different sets of complexes; and besides pure binary M(HL)_n²⁺ (HL is a neutral oxime), we found deprotonated M(HL)L⁺ as well as hydrolytic polynuclear H₋₆M₄(HL)₄²⁺ (M=Ni²⁺) and H₋₃M₂(HL)₂⁺ (M=Cu²⁺) species.



Our investigation of the metal-aminoacetamidoxime system has now been extended to include iminobis(acetamidoxime) (=L) ligand which contains two acetamidoxime groups on the central nitrogen atom.

The accurate structures of the complexes [NiL₂]Cl₂·2H₂O and [CuL₂]Cl₂ are known in the solid state.³ In both cases L is bound to the metal through its imine and oxime nitrogen atoms. The nickel complex is centrosymmetric and displays the octahedral coordination sphere (a), while the copper complex has a square-pyramidal structure (b) in which one ligand is tridentate and the other one bidentate.



The aim of the present study was to interpret the complexation in aqueous binary $H^+ - L$ and ternary $H^+ - Cu^{2+} - L$ and $H^+ - Ni^{2+} - L$ systems and to compare the results with those obtained previously for 2-aminoacetamidoximes. Our main concern is the existence of deprotonated and polynuclear species as well as the possible connection between the stabilities of the complexes in aqueous solution and the coordination modes in their solid phases.

EXPERIMENTAL

Iminobis(acetamidoxime), L, was prepared by the method presented by Eddy *et al.*⁴ The formula weight of the white air dried product as determined by potentiometric titration was 161.8 (calc. for $C_4H_{11}N_5O_2$ 161.2). M. p. 129–131 °C (lit.⁴ 126–127 °C).

The solid complex CuL_2Cl_2 was obtained by adding copper(II) chloride (0.01 mole) to a concentrated aqueous solution of L (0.02 mol) and filtering off the deep blue crystals formed after 3–4 h. Recrystallization was done from water. Analyses: Cu, Cl. The properties of the product were identical to those described by Eddy *et al.*⁴

The violet red $NiL_2(ClO_4)_2 \cdot 2\frac{1}{2}H_2O$ was prepared similarly to CuL_2Cl_2 using nickel(II)perchlorate hexahydrate instead of $CuCl_2$ as starting material. Analyses: Ni, ClO_4^- , H_2O .

Method. The present investigation was carried out as a series of potentiometric titrations at 25 °C and in a constant 1.0 M (Na)ClO₄ medium. The cell arrangement and the procedure to calibrate the glass electrode have been described in the preceding paper.¹

During the measurements the total concentrations of metal, C_M , and ligand, C_L , were varied within the limits $0.002 < C_M < 0.011$ M and $0.006 < C_L < 0.030$ M. In the presence of metal ions the titrations were generally performed at a constant C_L/C_M ratio and the free hydrogen ion concentration, h , was varied by adding perchloric acid or sodium hydroxide to the solution. In this way the ligand to metal ratios varying between $1 < C_L/C_{Cu} < 8$ and $1 < C_L/C_{Ni} < 4$ were studied. To obtain more data for the copper system at low values of the ligand number \bar{n} , some additional measurements with Cu^{2+} ions as the titrant were also carried out. In these titrations the ratio C_L/C_{Cu} varied between 2 and 0.7.

With copper(II) the formation of precipitates restricted the available $-\log h$ range to the upper limit of 7–8. In the nickel system the onset of precipitation occurs at somewhat higher pH and measurements up to pH *ca.* 11.8 were possible. Due to the reduced reliability of the glass electrodes at high pH levels, the $-\log h$ values greater than 9 were not, however, included in the final calculations.

The starting solutions were generally prepared by weighing in L to the metal perchlorate solution or by weighing in crystalline metal complexes to the ionic medium. Thus a double control of the analytical determinations of C_M and C_L was obtained.

Data treatment. For evaluation of the binary proton-ligand system the equilibrium constants are defined as follows (L is the neutral dioxime):



In the complexation of metal ions we assumed the presence of a three-component system of the form:



Table 1. Final values of the protonation and complex formation constants. The errors given are 3σ ($\log K$).

Reaction	$\log K$
$H^+ + L \rightleftharpoons HL^+$	5.858 ± 0.012
$2H^+ + L \rightleftharpoons H_2L^{2+}$	10.401 ± 0.018
$3H^+ + L \rightleftharpoons H_3L^{3+}$	10.9 ± 0.2
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	10.95 ± 0.09
$CuL^{2+} + L \rightleftharpoons CuL_2^{2+}$	3.81 ± 0.02
$CuL_2^{2+} \rightleftharpoons H_{-1}CuL_2^+ + H^+$	-2.95 ± 0.03
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	7.593 ± 0.015
$Ni^{2+} + 2L \rightleftharpoons NiL_2^{2+}$	14.655 ± 0.012
$NiL_2^{2+} \rightleftharpoons H_{-1}NiL_2^+ + H^+$	7.152 ± 0.018

In the calculation of the three-component systems the binary proton–ligand equilibrium (1) was assumed to be exactly known. The binary hydrolytic equilibria of copper(II) and nickel(II) ions could be neglected in the present study.

The mathematical analysis of the experimental data was performed with the least-squares computer programs MINQUAD-75⁵ and -76A⁶, which minimize the sum of the squares of residuals, $U = \Sigma(\Delta C_M^2 + \Delta C_L^2 + \Delta C_H^2)$, where C_M , C_L and C_H are the total concentrations of metal, ligand and proton, respectively. The computational work was performed on a Univac 1108 computer.

RESULTS AND DISCUSSION

The $H^+ - L$ system. The data used to evaluate the binary $H^+ - L$ equilibria comprise 5 titrations with 199 experimental points within the concentration ranges $0.006 \leq C_L \leq 0.030$ M. In the $-\log h$ range used here ($1.7 < -\log h < 9.0$) the neutral oxime ligand L can accept three protons: one on each of the amide nitrogens and one on the imine nitrogen. The corresponding equilibrium constants are shown in Table 1. The values of the stepwise protonation constants indicate that L and HL^+ are moderately strong bases ($\log k_1 = 5.86$ and $\log k_2 = 4.54$), while H_2L^{2+} with $\log k_3 \sim 0.5$ possesses no significant basicity. A comparison of the first two protonation steps with the respective steps in 2-aminoacetamidoximes¹ ($\log k_1 = 7.61 - 8.26$ and $\log k_2 = 1.76 - 2.47$) shows that the additional acetamidoxime group in L leads to a marked decrease in the basicity of the central imine nitrogen, and a marked increase in that of the amide nitrogen.

The acid strengths of the two oxime groups in L are very weak ($pK_a > 12$). The complex formation reactions studied here occur in considerably lower $-\log h$ regions, however, and the acidity constants referring to the oxime dissociations are not needed for the calculations of the speciations.

The $H^+ - Cu^{2+} - L$ system. Fig. 1 shows some of the experimental data visualized as the Bjerrum plot, $\bar{n}(\log[L])$. The value of \bar{n} is relatively high already at the lowest $\log[L]$ values. This implies that even at the lowest C_L/C_M quotients the complex CuL^{2+} is almost completely formed in all solutions from which reliable potential readings can be obtained, and further that it is not possible to calculate a very accurate value for the stability constant of the species CuL^{2+} . Moreover, the long horizontal region at \bar{n} -value 1 before \bar{n} starts to rise towards its limiting value 2 provides evidence for the much lower stability of the second

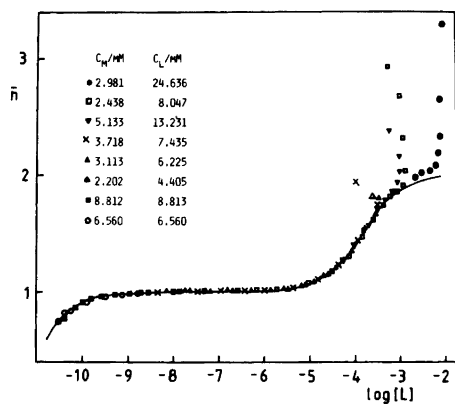


Fig. 1. Part of the experimental data for copper(II) plotted as curves $\bar{n}(\log[L])$. The concentrations given are start concentrations. The full curve has been calculated with the formation constants for the complexes CuL_2^{2+} and CuL_2^+ given in Table 1.

complex CuL_2^{2+} than CuL_2^+ . Thus a reliable value for the stepwise formation constant k_2 ($=\beta_{012}/\beta_{011}$) should be obtained.

The fact that \bar{n} -values greater than 1 do not fall on a single curve in Fig. 1 indicates the presence of deprotonated or polynuclear species in the system. Because the experimental data fulfilling the condition $C_H < 0$ cannot be visualized by the $\bar{n}(\log[L])$ -function only a part of these 'tails' can be presented in Fig. 1. In fact the accomplishment of the condition $C_H < 0$ is in itself a demonstration of the formation of deprotonated complex species in the system.

In the calculation it was soon found that the best additional complex was $\text{H}_{-1}\text{CuL}_2^+$. The total experimental data, comprising 9 titrations and 220 data points, could be quite satisfactorily explained merely by assuming the species CuL_2^{2+} , CuL_2^+ and $\text{H}_{-1}\text{CuL}_2^+$. The analysis ended at the R -value 0.0048 and because inclusion of any other deprotonated or polynuclear species in the model did not result in significantly better fit to the data, we accordingly suggest the above three complexes as the final model for complexation between Cu^{2+} and iminobis(acetamidoxime). The equilibrium constants with their standard deviations (3σ) are given in Table 1. In the calculations for Cu^{2+} the total concentrations of metal (C_M) and ligand (C_L) were given over the zero level CuL_2^{2+} . This strategy made it possible to obtain the value of the stepwise constant k_2 and trustworthy estimates for the errors involved in each of the constants directly from MINQUAD calculations.

Comparison of the stepwise formation constants of the complexes in Table 1 with the corresponding values reported for 2-aminoacetamidoximes shows L to be 10^2 – 10^4 times as strong a coordinating agent for Cu^{2+} ($\log \beta_{011}=10.95$) as 2-aminoacetamidoximes ($\log \beta_{011}=6.61$ – 8.79).² This is a consequence of L acting as tridentate ligand towards Cu^{2+} . The situation is quite different for the addition of the second ligand: here the $\log k_2$ -value 3.81 is even lower than the corresponding values for 2-aminoacetamidoximes ($\log k_2=4.68$ – 8.03).² The relationships between the stability constants make it tempting to suppose that bonding of L to CuL_2^{2+} occurs bidentately, and further that the complex CuL_2^{2+} has a similar structure in aqueous solution and in the solid state.

The complex CuL_2^{2+} contains four dissociable oxime protons. Additionally, the coordinated amide (or water) groups may show acidic properties. The only deprotonated complex species found here had the composition $\text{H}_{-1}\text{CuL}_2^+$. In the alkalimetric titrations the colour of the solution gradually changes from deep blue to dark green in the $-\log h$ range 6–8, which coincides with the $\text{p}K_a$ -value of CuL_2^{2+} (6.76). After the formation of $\text{H}_{-1}\text{CuL}_2^+$ is complete there is a large potential jump and a brownish precipitate separates. Possibly

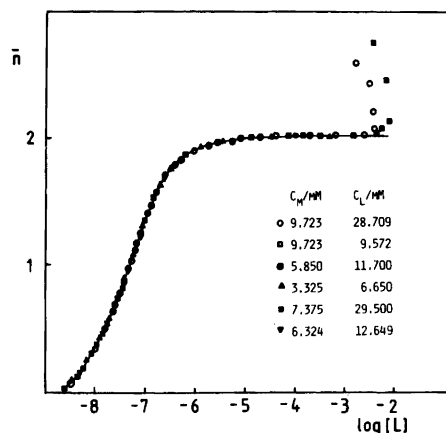


Fig. 2. Part of the experimental data for nickel(II) plotted as curves $\bar{n}(\log[L])$. The concentrations given are start concentrations. The full curve has been calculated with the formation constants for the complexes NiL^{2+} and NiL_2^{2+} given in Table 1.

coordination shifts occur during the deprotonation of the complex, but potentiometric data do not give any information about the actual structure of the hydrolytic species.

The $H^+ - \text{Ni}^{2+} - L$ system. The Bjerrum plot for Ni^{2+} in Fig. 2 is very different from that for Cu^{2+} . The complexes are distinctly less stable than those of Cu^{2+} and the two stepwise reactions in which L is successively coordinated to Ni^{2+} and NiL^{2+} are extensively overlapping. The limiting value of \bar{n} is 2 and the deviations from the single curve imply that there are at least some deprotonated species present in the system. The 'tails' in Fig. 2 appear only in titrations with higher C_L/C_{Ni} ratios. This is merely due to the fact that the formation of the bis complex is nearly complete before dissociation begins. Thus in most of the titrations the digression is not discovered with positive C_H values.

Calculations based on data from 7 different titrations with 230 experimental points showed the whole system to be best described in terms of the stepwise complexes NiL^{2+} and NiL_2^{2+} together with the deprotonated species $\text{H}_{-1}\text{NiL}_2^+$. The analysis ended at the R -value 0.0042 indicating a good fit.

The formation constants of the complexes given in Table 1 show NiL^{2+} and NiL_2^{2+} to be considerably higher in stability than the respective species of 2-aminoacetamidoximes ($\log \beta_{011} = 3.98 - 5.72$ and $\log \beta_{012} = 5.52 - 10.84$).¹ Unlike the case of Cu^{2+} the stepwise constants for the successive complexes, NiL^{2+} with $\log \beta_{011} = 7.59$ and NiL_2^{2+} with $\log k_2 = 7.06$, are of similar magnitude with most of the difference evidently due to statistical reasons. The results are in full agreement with those one could expect assuming tridentate bonding of L to Ni^{2+} and NiL^{2+} . Thus it is very likely that the structures of the complexes are octahedral with coordination through the imine and two oxime nitrogen atoms, as has been shown for solid $\text{NiL}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ in X-ray structure determination.³

The complex NiL_2^{2+} is violet-red both in aqueous solution and in the solid state. This colour remains practically unaltered upon deprotonation of the complex. The only deprotonated species verified in our conditions ($-\log h < 9$) had the composition $\text{H}_{-1}\text{NiL}_2^+$. The acidity constant $\text{p}K_a$ of NiL_2^{2+} is 7.50, and thus considerably higher than the corresponding value of the copper(II) complex (6.76).

Inspection of the titration data suggests that deprotonation of $\text{H}_{-1}\text{NiL}_2^+$ will occur at $-\log h$ values higher than 9 but a distinct inflection in the titration curve of Ni-L system at a metal to ligand ratio 1:2 at $-\log h \sim 9$ when formation of $\text{H}_{-1}\text{NiL}_2^+$ is completed indicates that the successive dissociation reactions are not overlapping. With nickel(II) it is very likely

that deprotonation occurs at the coordinated oxime groups but the alteration in the oxime function does not seem to result in any obvious changes in the coordination sphere.

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