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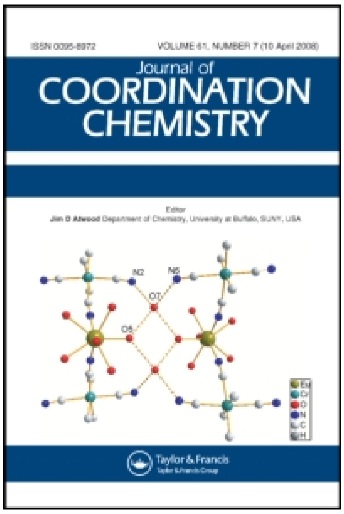

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# Equilibrium and structural studies of copper(II) and nickel(II) complexes with pyridine-2,6-diamidoxime in aqueous solution

MARKKU SALONEN*, HEIKKI SAARINEN and ILPO MUTIKAINEN

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The complex formation equilibria of copper(II) and nickel(II) with pyridine-2,6-amidoxime ($H_2L$) were studied in aqueous 0.1 M NaCl solution at 25°C by potentiometric titrations with use of a glass electrode. Experimental data were analyzed with the least-squares computer program SUPERQUAD to determine the complexes formed and their stability constants. The best model included both metal ions in the mononuclear complexes $M(H_2L)^{2+}$, $M(H_2L)_2^{2+}$, $M(H_2L)HL^+$ and $M(HL)_2$ and with nickel(II) also the complexes $Ni(HL)L^-$ and $NiL_2^{2-}$. The structure of the crystallized complex with the formula $[Ni(HL)_2] \cdot 4H_2O$ was determined by X-ray diffraction. The crystal structure is orthorhombic, space group *pbcn* with $a = 12.601(3)$, $b = 9.3990(19)$, $c = 17.195(3)$ Å, $\alpha = \beta = \gamma = 90°$ and $Z = 4$.

*Keywords*: Copper(II); Nickel(II); Pyridine-2,6-amidoxime complexes; Equilibria; Stability constants

## 1. Introduction

In earlier papers we described the equilibrium and structural studies of five pyridine-2-oximes [1–7] and some aliphatic amidoximes of type $RR'N(CH_2)_nC(NH_2)NOH$ [8, 9] with some divalent transition metal ions. These oximes are bidentate and coordinate to the divalent metal ions mainly through their pyridine or amine and oxime nitrogen atom forming five- or six-membered chelate rings. In the low pH range the oxime ligands coordinate as uncharged ligands but their oxime groups (NOH) deprotonate on increase of pH. The hydrolyzed complexes can polymerize through the oxime oxygen atoms and the amidoxime complexes also through the amido group in the form $-NH^{-}-$.

In this work we have expanded the equilibrium and structural studies of oxime complexes to the tridentate ligand pyridine-2,6-di(carbox)amidoxime ($H_2L$) with copper(II) and nickel(II) ions. This ligand has two deprotonable oxime groups. Bovenzi and Pearse [10] have reported the crystal structures of the solid ligand $H_2L$, $[Ni(H_2L)_2]SO_4 \cdot 5H_2O$ and $[Cu(H_2L)SO_4] \cdot 2H_2O$. To find out the role of the

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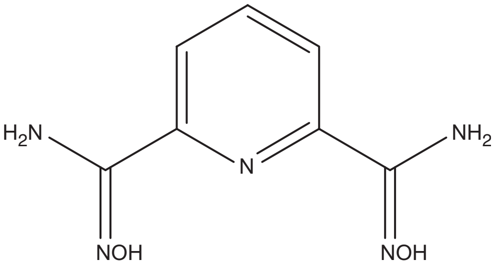
deprotonation of the oxime function on these complexes, the structure of $[Ni(HL)_2] \cdot 4H_2O$ has also been determined.



## 2. Experimental

### 2.1. *Reagents and solutions*

Pyridine-2,6-diamidoxime was synthesized by refluxing a suspension of 6.28 g hydroxylamine hydrochloride, 3.62 g NaOH and 5.0 g 2,6-dicyanopyridine (97%, Aldrich) in 1 : 1 ethanol/water solution according to the method described by Banks and Brookes [11]. The white crystalline product was poorly soluble in water and common organic solvents. It was recrystallized from an aqueous HCl solution as dihydrochloride. The recrystallized product was dissolved in deionized water, and the exact hydrochloride (HCl) concentration of the prepared solution (0.112 M) was determined by NaOH titration.

The solutions of the metal chlorides were standardized against standard EDTA. The concentration of Cu(II) was also determined electrogravimetrically and that of Ni(II) by precipitation with dimethylglyoximate.

The brownish complex of formula $Ni(HL)_2(H_2O)_2$ was isolated in the solid state by adjusting the pH of the solution containing $NiCl_2$ and ligand in 1 : 2 molar ratios to about 9 with NaOH.

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### 2.2. *Potentiometric measurements and data treatment*

Investigation of the complex formation equilibria was carried out as a series of potentiometric titrations in aqueous 0.1 M NaCl solutions at 25.0°C. Because of the poor solubility of some of the most interesting complexes in perchlorate solutions, NaCl was chosen as inert salt instead of the more common $NaClO_4$. The electrode system used in the measurements has been described earlier [8]. Ratios of the total concentrations of metal ion, $C_M$, to ligand, $C_L$, were held constant during the measurements. Before each separate titration the potentiometer was calibrated to hydrogen ion concentration, $h$, by titration of 50 mL 0.1 M NaCl solution with 7 mL exactly known 0.1 M HCl solution, and the known amount of metal ion and ligand added to this solution. The available concentration and pH ($= -\log h$) ranges were defined by the formation of a precipitate or by very slow attainment of equilibrium.

In evaluating the equilibrium constants the binary two-component equilibria (1–7) were considered:

$$H_2L + H^+ \Omega H_3L^+; \beta_{101} \tag{1}$$

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$$H_2L + 2H^+ \, \Omega \, H_4L^{2+}; \beta_{201} \tag{2}$$

$$H_2L \, \Omega \, H^+ + HL^-; K_{a1} \tag{3}$$

$$HL^- \, \Omega \, H^+ + L^{2-}; K_{a2} \tag{4}$$

$$pH^+ + qM^{2+} \, \Omega \, (H^+)_p(M^{2+})_q; \beta_{pq0} \tag{5}$$

$$M^{2+} + H_2L \, \Omega \, M(H_2L)^{2+}; K_1 \tag{6}$$

$$M(H_2L)^{2+} + H_2L \, \Omega \, M(H_2L)_2^{2+}; K_2 \tag{7}$$

The acid strengths of the oxime groups are very weak, and thus the values of the p$K_{a1}$ and p$K_{a2}$ in reactions (3) and (4) are not very accurate. This is the reason to choose the ligand as a component in the form of the uncharged oxime ($H_2L$) in evaluating the stability constants of a three-component ($H^+$, $M^{2+}$ and $H_2L$) system:

$$pH^+ + qM^{2+} + rH_2L \, \Omega \, (H^+)_p(M^{2+})_q(H_2L)_r; \beta_{pqr} \tag{8}$$

In the evaluation of the three-component experimental data the equilibrium constants of reactions (1)–(5) were considered as known. For the binary hydrolytic equilibria of copper(II) and nickel(II), we used the log $\beta_{-110}$ values −8.3 and −9.26, respectively [12]. No attention was paid to the possible formation of chloro complexes.

The mathematical analysis of data was performed with the least-squares computer program SUPERQUAD [13]. The *pqr* triplets and corresponding equilibrium constants that best fit the experimental data were determined by minimizing the error sum $U = 3w_i(E_i^{\mathrm{Obs}} - E_i^{\mathrm{Calcd}})^2$. The weighting factor $w_i$ is determined by the equation $w_i = 1/(\sigma_E{}^2 + \delta E_i/\delta V_i)\sigma_V{}^2$, where $\sigma_E$ (=0.1 mV) and $\sigma_V$ (=0.02 mL) are the estimated uncertainties in the electrode and titrant (NaOH) volume readings and $\delta E_i/\delta V_i$ is the slope of the titration curve. The criteria for choosing the best fit to the experimental data were $\chi^2$ statistics and the sample standard deviation, $s$ [14].

### 2.3. *X-ray crystallographic analysis and data collection*

A crystal was selected for the X–ray measurements and mounted to the glass fiber using the oil drop method [15]; data were collected at 173 K on a Nonius KappaCCD diffractometer (Mo-K$\alpha$ radiation, graphite monochromator, $\lambda = 0.71073$). The intensity data were corrected for Lorentz and polarization effects and for absorption. The programs COLLECT [16], SHELXS–97 [17] and SHELXL–97 [18] were used for data reduction, structure solution and structure refinement, respectively. The nonhydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The H atoms of the water molecules were determined from the difference map. One of the water molecules was disordered. Details of the X-ray diffraction studies are listed in table 1.

The bond lengths and angles of interest are collected in table 2. The numbering of the atoms can be seen in figure 1. Lists of the structure factors and anisotropic temperature factor are available from the authors on request.

Table 1. Crystal data and structure refinement for $[Ni(HL)_2]\cdot 4H_2O$.

| | |
|---|---|
| Identification code | *pbcn* |
| Empirical formula | $C_{14}H_{24}N_{10}NiO_8$ |
| Formula weight | 519.14 |
| Temperature (K) | 173(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | *pbcn* |
| Unit cell dimensions (Å, °) | |
| $a$ | 12.601(3) |
| $b$ | 9.3990(19) |
| $c$ | 17.195(3) |
| $\alpha$ | 90 |
| $\beta$ | 90 |
| $\gamma$ | 90 |
| Volume (Å$^3$) | 2036.5(7) |
| $Z$ | 4 |
| $D_{calcd}$ (Mgm$^{-3}$) | 1.693 |
| Absorption coefficient (mm$^{-1}$) | 1.022 |
| $F(000)$ | 1080 |
| Crystal size (mm$^3$) | 0.20 × 0.10 × 0.10 |
| $\theta$ Range for data collection (°) | 2.87–27.55 |
| Index ranges | $-16 \le h \le 16$, $-12 \le k \le 12$, $-22 \le l \le 22$ |
| Reflections collected | 62,957 |
| Independent reflections | 2358 [$R_{int} = 0.0682$] |
| Completeness to $\theta = 27.55°$ | 99.9% |
| Max. and min. transmission | 0.9047 and 0.8217 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2358/5/197 |
| Goodness-of-fit on $F^2$ | 1.029 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0290$, $wR_2 = 0.0701$ |
| $R$ indices (all data) | $R_1 = 0.0416$, $wR_2 = 0.0759$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.331 and −0.408 |

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## 3. Results and discussion

To visualize the experimental results for copper(II) and nickel(II) complexation sets of $Z_H$ *versus* pH were calculated. These plots are shown in figure 2. $Z_H$ is defined as the average number of $OH^-$ ions reacted per ligand ($H_2L$) $Z_H = (h - C_H - K_w h^{-1})/C_L$, where $C_H$ denotes the total concentration of hydrogen ion calculated over the zero level $H_2L$, $H_2O$ and $M^{2+}$.

### 3.1. *The protonation and acidity constants of the ligand*

To determine the values of the protonation and acidity constants the ligand added to the acidic solution described above was titrated with an accurately known NaOH solution. Only dilute solutions of the ligand could be used without precipitation. In solutions with initial $C_L = 3$ mM a white precipitate, which was formed already at pH 3−4, dissolved again in the pH range 10−11. Titration points after the dissolution had to be used in data treatment for determination of the acidity constants $K_{a1}$ and $K_{a2}$. The protonation and acidity constants calculated from 246 titrations points of the five titrations with $\chi^2 = 8.37$ and $s = 1.75$ are shown in table 3. The values of constants log $\beta_{101} = 3.817$ and p$K_{a1} = 11.2$ prove that the precipitate was formed by the uncharged ligand $H_2L$. Bovenzi and Pearse [10] have shown with infrared stretching assignments of

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Table 2. Selected bond lengths (Å) and angles (°) for $[Ni(HL)_2]\cdot 4H_2O$.

| | |
|---|---|
| Ni(1)–N(10) | 2.0042(14) |
| Ni(1)–N(10)#1 | 2.0042(14) |
| Ni(1)–N(1) | 2.1326(14) |
| Ni(1)–N(1)#1 | 2.1326(14) |
| Ni(1)–N(9) | 2.1361(15) |
| Ni(1)–N(9)#1 | 2.1361(15) |
| N(1)–C(2) | 1.301(2) |
| N(1)–O(11) | 1.4239(18) |
| C(2)–N(12) | 1.344(2) |
| C(2)–C(3) | 1.497(2) |
| C(3)–N(10) | 1.344(2) |
| C(3)–C(4) | 1.394(2) |
| C(4)–C(5) | 1.397(3) |
| C(5)–C(6) | 1.393(3) |
| C(6)–C(7) | 1.393(2) |
| C(7)–N(10) | 1.349(2) |
| C(7)–C(8) | 1.476(2) |
| C(8)–N(9) | 1.305(2) |
| C(8)–N(13) | 1.374(2) |
| N(9)–O(14) | 1.3752(17) |
| N(10)–Ni(1)–N(10)#1 | 177.28(8) |
| N(10)–Ni(1)–N(1) | 75.76(6) |
| N(10)#1–Ni(1)–N(1) | 102.38(5) |
| N(10)–Ni(1)–N(1)#1 | 102.38(5) |
| N(10)#1–Ni(1)–N(1)#1 | 75.76(6) |
| N(1)–Ni(1)–N(1)#1 | 96.44(8) |
| N(10)–Ni(1)–N(9) | 77.36(5) |
| N(10)#1–Ni(1)–N(9) | 104.42(5) |
| N(1)–Ni(1)–N(9) | 153.08(5) |
| N(1)#1–Ni(1)–N(9) | 87.70(6) |
| N(10)–Ni(1)–N(9)#1 | 104.42(5) |
| N(10)#1–Ni(1)–N(9)#1 | 77.36(5) |
| N(1)–Ni(1)–N(9)#1 | 87.70(6) |
| N(1)#1–Ni(1)–N(9)#1 | 153.08(5) |
| N(9)–Ni(1)–N(9)#1 | 100.56(8) |
| C(2)–N(1)–O(11) | 110.93(13) |
| C(2)–N(1)–Ni(1) | 117.15(11) |
| O(11)–N(1)–Ni(1) | 131.62(10) |
| N(1)–C(2)–N(12) | 126.05(16) |
| N(1)–C(2)–C(3) | 113.53(15) |
| N(12)–C(2)–C(3) | 120.41(15) |
| N(10)–C(3)–C(4) | 121.12(16) |
| N(10)–C(3)–C(2) | 112.93(14) |
| C(4)–C(3)–C(2) | 125.95(16) |
| C(3)–C(4)–C(5) | 117.94(16) |
| C(6)–C(5)–C(4) | 120.59(16) |
| C(5)–C(6)–C(7) | 118.26(17) |
| N(10)–C(7)–C(6) | 120.81(16) |
| N(10)–C(7)–C(8) | 113.72(14) |
| C(6)–C(7)–C(8) | 125.42(15) |
| N(9)–C(8)–N(13) | 124.38(16) |
| N(9)–C(8)–C(7) | 115.73(15) |
| N(13)–C(8)–C(7) | 119.55(15) |
| C(8)–N(9)–O(14) | 115.26(14) |
| C(8)–N(9)–Ni(1) | 114.45(11) |
| O(14)–N(9)–Ni(1) | 129.42(10) |
| C(3)–N(10)–C(7) | 121.22(15) |
| C(3)–N(10)–Ni(1) | 120.37(11) |
| C(7)–N(10)–Ni(1) | 118.40(11) |

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $y$, $-z+1/2$.

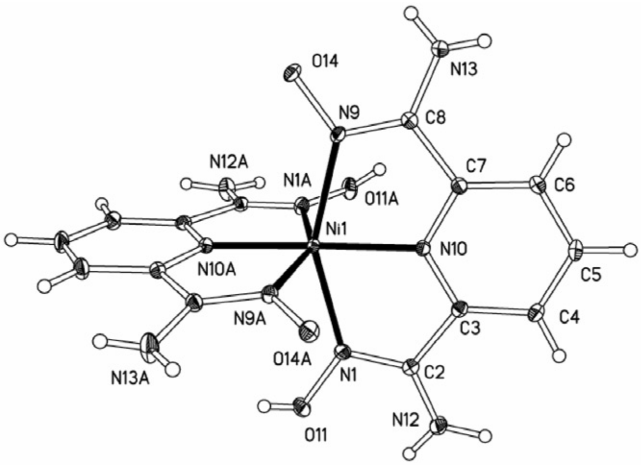

Figure 1. Crystal structure of $[Ni(HL)_2] \cdot 4H_2O$ showing the atomic numbering scheme. The water molecules have been omitted for clarity.

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$NH_2$ and OH groups that in the solid state there are considerable intermolecular hydrogen bonds between the adjacent ligand molecules ($H_2L$) involving amide and oxime hydrogens with oxime oxygens ($N\text{–}H \cdots O$ and $O\text{–}H \cdots O$) and with amide nitrogens ($N\text{–}H \cdots N$ and $O\text{–}H \cdots N$). Every uncharged ligand molecule ($H_2L$) has four groups capable of intermolecular hydrogen bonding, which probably promotes the precipitation.

### 3.2. *The copper(II) complexes*

Complex formation occurs in very acidic conditions. At the beginning of the measurements the solutions were blue or blueish-green and during titration the green color strengthened. Figure 2 shows very strong complex formation already at pH ca. 2. The same was true in the system $Cu^{2+}$–pyridine-2-amidoxime [3]. Here the stability constant of the mono complex $Cu(H_2L)^{2+}$ could be determined only by using very dilute solutions with $C_M = 0.347\text{–}0.681$ mM and $C_L = 0.347\text{–}0.689$ mM in 1 : 1 titrations. The best fit to the data from eight titrations and 208 points ($\chi^2 = 36.7$ and $s = 1.02$) was obtained with a simple model consisting of the mononuclear species $Cu(H_2L)^{2+}$, $Cu(H_2L)_2^{2+}$, $Cu(H_2L)HL^+$ and $Cu(HL)_2$ (or $Cu(H_2L)L_2$). The stability constants are given in table 3. The useful experimental data were restricted to pH < 6.8, preventing further analysis.

Because of the high stability of $Cu(H_2L)^{2+}$ no accurate value of $\beta_{011}$ could be obtained. The values of the other $\beta$-constants calculated seemed to be affected by the given $\beta_{011}$ value and sensitive to its systematic errors, but the stepwise stability and acidity constants of $Cu(H_2L)_2{}^{2+}$ reported in table 3 were practically independent of the $\beta_{011}$ value (in the wide prefixed log $\beta_{011}$ range 6.4–7.0) and more precise. An example of the concentration distribution of the copper(II) species is shown in figure 3. The computer program SPE was used in these calculations [19].

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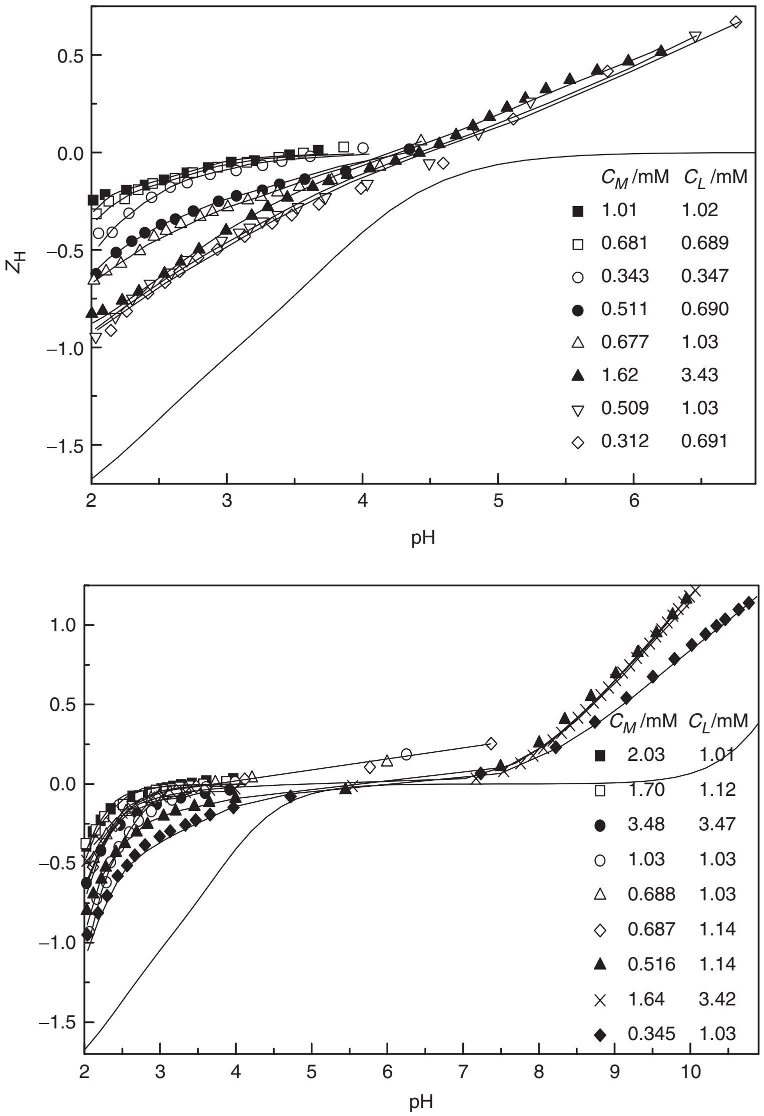

Figure 2. A portion of the experimental data plotted as curves $Z_H$ *vs*. pH for copper(II) (top) and nickel(II) (below) complex formation with pyridine-2,6-diamidoxime $H_2L$. The full lines have been calculated using the proposed stability constants in table 3. The lowest line refers to the ligand alone.

### 3.3. *The nickel(II) complexes*

Figure 2 shows measurable complex formation at the beginning of the measurements, where the solutions were almost colorless. In the course of the titration the solutions had weak violet tone but after neutralization of the added acid they became yellow, later light brown and in the pH range 9–10 turned dark brown. The best fit to the experimental data from 265 points/9 titrations ($\chi^2 = 28.2$, $s = 1.07$) was obtained by assuming the mononuclear species $Ni(H_2L)^{2+}$, $Ni(H_2L)_2^{2+}$, $Ni(H_2L)HL^+$, $Ni(HL)_2$,

Table 3. Proposed formula and stability constants (log $\beta_{pqr}$) of the pyridine-2,6-diamidoxime complexes relating to the reaction $p\text{H}^+ + q\text{M}^{2+} + r\text{H}_2\text{L}\ \Omega\ (\text{H}^+)_p(\text{M}^{2+})_q(\text{H}_2\text{L})_r$ and their first acidity constants (p$K_a$) in aqueous 0.1 M NaCl solution at 25°C.

| *p q r* | Proposed formula | log $\beta_{pqr} \pm 3\ \sigma$ | p$K_a \pm 3\sigma$ |
|---|---|---|---|
| 1 0 1 | $H_3L^+$ | $3.817 \pm 0.015$ | $3.817 \pm 0.015$ |
| 2 0 1 | $H_4L^{2+}$ | $6.153 \pm 0.013$ | $2.336 \pm 0.013$ |
| −1 0 1 | $HL^-$ | $-11.2 \pm 0.2^a$ | $12.2 \pm 0.2^a$ |
| −2 0 1 | $L^{2-}$ | $-23.4 \pm 0.2^a$ | |
| 0 1 1 | $Cu(H_2L)^{2+}$ | $6.66 \pm 0.13$ | |
| 0 1 2 | $Cu(H_2L)_2^{2+}$ | $3.53^b \pm 0.04$ | $4.92 \pm 0.05$ |
| −1 1 2 | $Cu(H_2L)(HL)^+$ | $5.23 \pm 0.15$ | $6.71 \pm 0.12$ |
| −2 1 2 | $Cu(HL)_2$ (or $Cu(H_2L)L$) | $-1.48 \pm 0.20$ | |
| 0 1 1 | $Ni(H_2L)^{2+}$ | $5.67 \pm 0.15$ | |
| 0 1 2 | $Ni(H_2L)_2^{2+}$ | $11.31 \pm 0.08$ | $8.17 \pm 0.04$ |
| −1 1 2 | $Ni(H_2L)(HL)^+$ | $3.14 \pm 0.09$ | $9.18 \pm 0.04$ |
| −2 1 2 | $Ni(HL)_2$ | $-6.04 \pm 0.09$ | $9.96 \pm 0.05$ |
| −3 1 2 | $Ni(HL)L^-$ | $-16.00 \pm 0.10$ | $11.25 \pm 0.22$ |
| −4 1 2 | $NiL_2^{2-}$ | $-27.25 \pm 0.23$ | |

[a] ± 10 $\sigma$. [b] = log $K_2$ relating to the reaction $Cu(H_2L)^{2+} + H_2L\ \Omega\ Cu(H_2L)_2^{2+}$.

$Ni(HL)L^-$ and $NiL_2^{2-}$. The stability constants and the acidity constants of $Ni(H_2L)_2^{2+}$ are given in table 3.

For nickel(II) the stability constant of the mono complex is fairly inaccurate but unlike the copper(II) complexes, the inaccuracy is not markedly cumulated to the other $\beta$-constants calculated. The overall stability constants of $Ni(H_2L)_2^{2+}$, $Ni(H_2L)HL^+$, $Ni(HL)_2$ and $Ni(HL)L^-$ could be exactly determined in the pH range 8–10. Such accuracy for the stability constant of $NiL_2^{2-}$ could not be obtained, because the complex was observed only in solutions in the pH range >9.7 and in the calculations it was necessary to use data points up to pH 11.0. An example of the concentration distribution of the nickel(II) species is shown in figure 3.

### 3.4. *The crystal structure of the solid nickel(II) complex*

The crystal structure of the solid $Ni(HL)_2$ confirms that two tridentate ligands are approximately perpendicularly coordinated to each other. The nickel(II) ion is six-coordinate through the oxime, oximato and heterocyclic nitrogens of the two ligands. The resulting configuration is a slightly distorted octahedron, the distortion rising from the rigid structures of the ligands. The N(1)–Ni–N(9) angle (153.05°) is approximately equal to the sum of the angles N(10)–Ni–N(1) and N(10)–Ni–N(9) (153.12°), proving a planar coordination by both ligands. The two Ni–N (imine) bond lengths are essentially equivalent but shorter than the four other Ni–N bonds, consistent with the results of the crystal structure of $[Ni(H_2L)_2]SO_4 \cdot 5H_2O$ by Bovenzi and Pearse [10]. The N–O bonds are clearly shorter than the N–O(H) bonds, and the C=N–O angles (115.26°) are clearly greater than the C=N–O(H) angles (110.93°). Unexpectedly, there is no essential difference between the Ni–N (oxime) and Ni–N (oximato) bond lengths.

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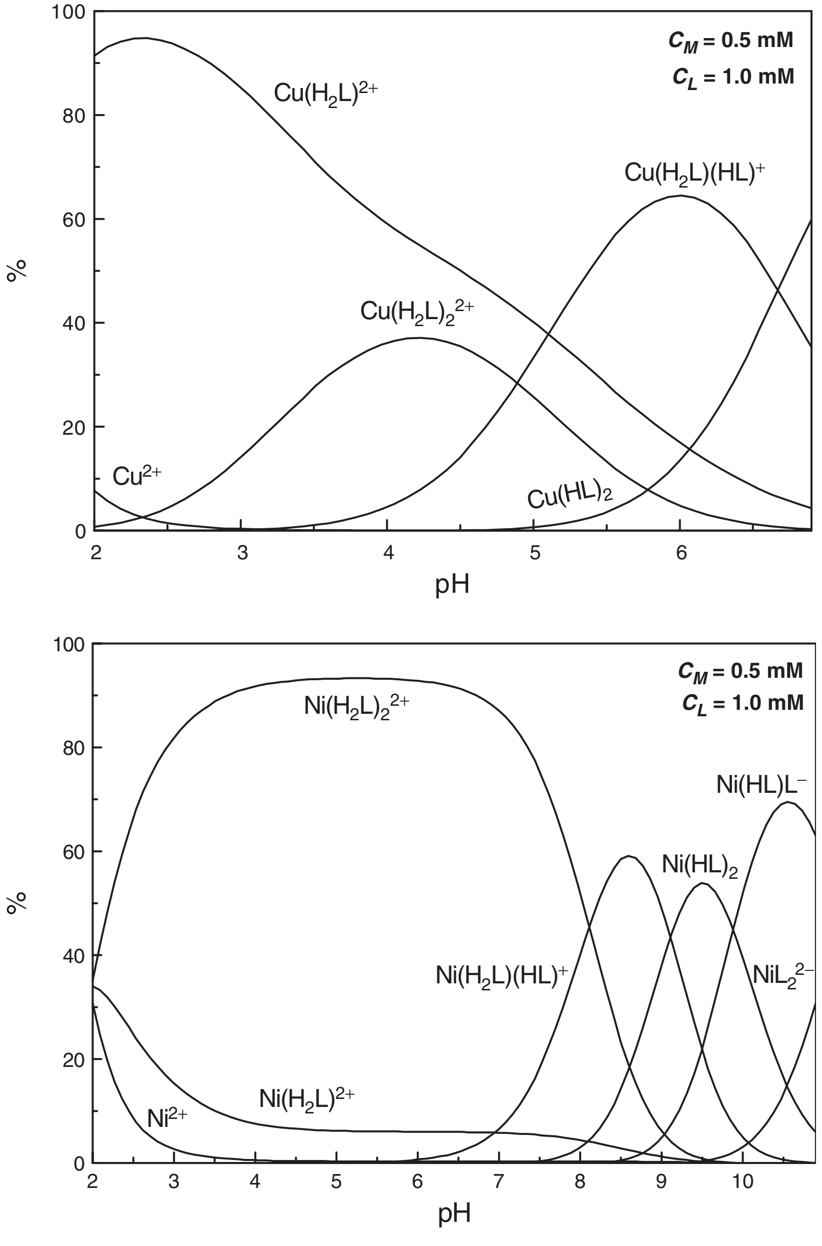

Figure 3. Examples of the concentration distributions of the copper(II) and nickel(II) species *vs.* pH.

### 3.5. *Discussion*

The uncharged pyridine-2,6-diamidoxime ligand ($H_2L$) is a very weak acid. Its first acidity constant ($pK_{a1} = 11.2$) is about one log unit greater than the second ($pK_{a2} = 12.2$) and about a half log unit greater than the acidity constant of the

Table 4. Protonation and acidity constants (log $\beta_{101}$, p$K_{a1}$ and p$K_{a2}$, respectively) of pyridine-2,6-diamidoxime and some related compounds in aqueous solution at 25°C.

| Ligand or complex | log $\beta_{101}$ | p$K_{a1}$ | p$K_{a2}$ | Medium[a] | Reference |
|---|---|---|---|---|---|
| Pyridine-2,6-diamidoxime ($H_2L$) | 3.829 | 11.2 | 12.2 | 0.1 M NaCl | This work |
| Pyridine-2-amidoxime (Hpam) | 3.798 | 11.7 | | 0.1 M NaCl | 3 |
| Pyridine-2,6-dialdoxime ($H_2$pda) | 2.18 | 9.47 | 10.21 | 0.5 M ($NaNO_3$)[b] | 20 |
| $H_2$pda | | 10.00 | 10.63 | 0.05 M ($NaClO_4$) | 21 |
| $H_2$pda | 2.34[c] | 9.7 | 10.7 | 0.01 M ($NaClO_4$) | 22 |
| Pyridine-2-aldoxime (Hpa) | 3.48 | 10.17 | | $I < 0.001$ M | 23 |
| Hpa | 3.590 | 10.01 | | 0.1 M NaCl | 4 |
| Hpa | 3.865 | 9.922 | | 1.0 M NaCl | 5 |
| $Ni(Hpa)_2^{2+}$ | | 4.82 | 6.47 | 1.0 M NaCl | 5 |
| $Ni(Hpa)_3^{2+}$ | | 4.84 | 6.28 | 1.0 M NaCl | 5 |
| $Ni(Hpam)_2^{2+}$ | | 7.76 | 8.60 | 0.1 M NaCl | 3 |
| $Ni(Hpam)_3^{2+}$ | | 8.23 | 9.68 | 0.1 M NaCl | 3 |
| $Ni(H_2L)_2^{2+}$ | | 8.17 | 9.18 | 0.1 M NaCl | This work |
| $Ni(HL)_2$ | | 9.96 | 11.3 | 0.1 M NaCl | This work |
| $Ni(Hpda)_2$ | | 7.3 | 8.9 | 0.01 M ($NaClO_4$) | 22 |

[a] Ionic strength ($I$, the background electrolyte is in brackets). [b] 20°C. [c] $I = 0.005$ M ($NaClO_4$).

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uncharged pyridine-2-carboxoxime (p$K_a = 11.7$). Comparable acidity differences are found between the free pyridine-2,6-dialdoxime (p$K_{a1} = 9.7$ and p$K_{a2} = 10.7$) and pyridine-2-aldoxime (p$K_a = 10.17$) ligands [20–23]. The free amidoximes seem to be about 1.5 p$K_a$ units weaker acid than the correspondent aldoximes table 4.

The protonation constant of pyridine-2,6-dialdoxime (log $\beta_{101} = 2.34$) is more than one log unit smaller than that of pyridine-2-aldoxime (3.48) [22, 23], but no clear difference exists between the protonation constants of pyridine-2,6-diamidoxime (log $\beta_{101} = 3.817$) and pyridine-2-amidoxime (3.798). Pyridine-2,6-diamidoxime has two amide groups capable of protonation, but due to their short distance from the nearby pyridine nitrogen the acid strengths of the protonated amide $–NH_3{}^+$ groups are very high. In the pH range 2–3 only one amide group is partly protonated with p$K_a = 2.336$.

The stability constant of $Cu(H_2L)^{2+}$ is very high (log $K_1 = 6.66$) but the stepwise stability constant of $Cu(H_2L)_2{}^{2+}$ is much smaller (log $K_2 = 3.53$). This is caused by the Jahn–Teller distortion of the octahedral copper(II) complexes. In the solid state Bovenzi and Pearse [10] reported that the reaction of pyridine-2,6-diamidoxime with copper(II) sulfate does not give the expected monomeric product but rather a two-dimensional linear Jahn–Teller distorted polymer $\{[Cu(H_2L)SO_4] \cdot 2H_2O\}_n$. Each of the copper–ligand units are bonded to two sulfate groups by Cu–O bonds resulting in five-coordinate copper(II) atoms. Our attempts to synthesize any crystalline mono and *bis* complex with copper(II) chloride were unsuccessful. Also, Bovenzi and Pearse [10] reported unsuccessful attempts to synthesize a non-polymer mono complex and any *bis* complex with copper(II) sulfate.

The Jahn–Teller distortion also weakens the acidity of the ligand coordinated on the $z$ axis, explaining the rather large difference between the values of p$K_{a1} = 4.92$ and p$K_{a2} = 6.71$. Figure 1 shows that in $NiH_2L_2$ both ligands are present in the form $HL^-$ giving the structure $Ni(HL)_2$. In the case of the copper(II) complex $Cu(H_2L)HL^+$, deprotonation to $Cu(HL)_2$ is questionable; it is also possible that both of the protons dissociate from the same ligand in the $xy$ plane giving a complex

$Cu(H_2L)L$. Pinart *et al.* [20] have proposed that the structure of the corresponding pyridine-2,6-dialdoxime complex is $Cu(HL)_2$ with intramolecular hydrogen bonding ($=N–O–H \cdots {}^{-}O–N=$) between the adjacent oxime and oximato groups. Many bidentate oximes (HL) form such intramolecular hydrogen bridges in octahedral deprotonated *bis* complexes of type $M(HL)L^+$, if the oxime and oximato groups are *cis*-oriented in a plane [24]. In the solid pyridine-2,6-carboxamidoximato complex $Ni(HL)_2$ no intramolecular hydrogen bridges can be observed between the oxime and oximato groups of the perpendicularly coordinated ligands, nor between the adjacent oxime NOH and amide $NH_2$ groups ($=N–O–H \cdots NH_2–$). In the copper(II) complexes $Cu(H_2L)HL^+$ and $Cu(HL)_2$, Jahn–Teller distortion can cause such a marked deviation on the $z$ axis to the ligand that some intramolecular hydrogen bonding is possible. It may be noted that no deprotonated mono complexes such as $Cu(HL)^+$ and $Ni(HL)^+$ could be observed. In a weaker ligand field the mono complexes $Cu(H_2L)^{2+}$ and $Ni(H_2L)^{2+}$ are surely weaker acids than the *bis* complexes $Cu(H_2L)_2{}^{2+}$ ($pK_{a1} = 4.92$) and $Ni(H_2L)_2^{2+}$ ($pK_{a1} = 8.17$). However, the absence of $Cu(HL)^+$ even in the pH range 6.0–6.7 can be due to forming of deprotonated *bis* complexes $Cu(H_2L)HL^+$ and $Cu(HL)_2$ with some intramolecular hydrogen bonding stabilizing the complex.

In the case of nickel(II) the stepwise stability constant of $Ni(H_2L)_2^{2+}$ ($\log K_2 = 5.64$) is nearly equal to that of $Ni(H_2L)^{2+}$ ($\log K_1 = 5.67 \pm 0.15$). As with many other amidoxime complexes of $Ni^{2+}$ and $Co^{2+}$, the stability relations of $(K_3) : K_2 : K_1$ are clearly greater than the statistic stability relations of the octahedral complexes [1–9]. Similar effect has been found for pyridine-2-aldoxime and its methylated derivatives (6-methylpyridine-2-aldoxime and 1-(2-pyridinyl)etanone oxime). This is due to strengthening of the ligand field in the formation of the *bis* and *tris* complexes. The strengthening of ligand field in the stepwise complex formation through spin pairing can cause an abnormal stability order. For example, for 2,2′-bipyridyl and 1,10-phenantroline complexes $FeL^{2+}$, $FeL_2^{2+}$ and $FeL_3^{2+}$, where the aqueous mono and *bis* complexes are high spin and the *tris* complexes low spin, the stability orders are $K_3 > K_1 > K_2$ [25, 26] with $\log (K_3/K_2) = 5.75$ and 4.78, respectively [26]. In formation of the octahedral nickel(II) complex $Ni(H_2L)_2^{2+}$ from $Ni(H_2L)^{2+}$ the ligand field can be strengthened without spin pairing because of the structure of $d^8$ ($t_{2g}{}^6 e_g{}^2$). The great inaccuracy of $\log K_1$ is due to the appearance of $Ni(H_2L)_2^{2+}$ already in beginning of the measurements in the pH range 2–3.

The titration and crystallographic analyses (figure 1) show that the *bis* complex $Ni(H_2L)_2^{2+}$ dissolves with increasing pH stepwise to $Ni(HL)_2$, which further dissolves to $NiL_2^{2-}$. The acidity constants of $Ni(HL)_2$ ($K_{a3}$ and $K_{a4}$ of $Ni(H_2L)_2^{2+}$) are 2–3 log units smaller than those of the corresponding pyridine-2,6-dialdoxime complex table 4. The same trend is also observed for many corresponding pyridine-2-amidoxime and pyridine-2-aldoxime complexes of $Ni^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ [1–6]. This is apparently due to the weaker acidities of the oxime NOH groups of the amidoxime ligands as noted above. As in the solid $Ni(HL)_2$ intramolecular hydrogen bonding between the adjacent oxime NOH and amide $NH_2$ groups of these ligands are improbable in water. It also must be noted that the ketoxime 1-(2-pyridinyl)ethanone oxime is a weaker acid ($pK_a = 10.87$) than pyridine-2-aldoxime ($pK_a = 10.01$) but stronger than pyridine-2-amidoxime ($pK_a = 11.7$) [3, 4]. The methyl group of the ketoxime cannot form an intramolecular hydrogen bridge with the NOH group but it can shield the oxime group from attack by water. The amide groups of amidoximes can shield in a similar way but also by hydrogen bonding with the water.

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It is unexpected that in the solid $Ni(HL)_2$ no differences between the Ni–N (oxime) and Ni–N (oximato) bond lengths (2.1326(14) and 2.1361(15) Å, respectively) can be observed. The N–O bonds (1.3752(17) Å) are shorter than the N–O(H) bonds (1.4239(18) Å), but the negative charge of oxygen atom tends to distribute to the adjacent N atom. On the other hand, the displacement of the proton leads to opening of the C=N–O angles, which closes both the adjacent Ni–N–O and Ni–N=C angles and seems to affect the whole ligand geometry. For example, in $Ni(HL)_2$ the C=N–O(H) and C=N–O angles are 110.9(1)° and 115.3(1)°, respectively. The C(2)–N(1)–Ni(1) and C(8)–N(9)–Ni(1) angles are 117.15(11)° and 114.45(11)°, respectively, but in $Ni(H_2L)_2^{2+}$ the corresponding angles are 116.3(2)° [10]. In general, the C=N–O angles and the N–O bond lengths in nickel(II) amidoximato complexes are 115–120° and 1.261–1.357 Å [27–29], in copper(II) and nickel(II) amid- and ketoxime complexes 112–115° and 1.415–1.438 Å [30–33] and in free amidoximes 109–112° and 1.385–1.415 Å [33–38]. Only with bidentate oxime ligand are the reported $Ni^{2+}$–N (oximato) bonds (2.007–2.009 Å) [27, 28] clearly shorter than the $Ni^{2+}$–N (oxime) bonds (2.106–2.135 Å) [30, 31]. The tridentate dioxime and the polydentate oximes [29, 31] are more rigid than the bidentate oxime ligands and the shortening of the Ni–N bonds by displacement of the oxime proton are hindered by steric factors.

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