COMPLEX FORMATION OF PYRIDINE OXIMES WITH DIVALENT TRANSITION METAL IONS IN AQUEOUS SOLUTION

MARKKU A. J. SALONEN

Department of Chemistry
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation

To be presented with permission of the Faculty of Science of the University of Helsinki for public criticism in Auditorium A 129 of Department of Chemistry, A. I. Virtasen aukio 1, on December 16th at 12 o’clock noon.

Helsinki 2020
Supervisor

Professor Timo Repo
Department of Chemistry
University of Helsinki
Finland

Reviewers

Professor Konstantin Popov
Laboratory head of JSC “Fine Chemical R&D Centre”
Moscow, Russian Federation

Professor Mika Sillanpää
University of Johannesburg
South Africa

Opponent

Docent Ari Lehtonen
University of Turku
Finland

© Markku A. J. Salonen
ISBN 978-951-51-6898-6 (PDF)
http://ethesis.helsinki.fi

Unigrafia
Helsinki 2020
ABSTRACT

The complex formation equilibria of pyridine-2-aldoxime and its methyl or amido derivatives (HL) with cobalt(II), zinc(II), and cadmium(II) ions, and the protonation and complex formation equilibria of pyridine-2,6-carboxamidoxime (H2L) with copper(II) and nickel(II) ions were studied in aqueous 0.1 M Na(Cl) solution at 25 °C by potentiometric titrations with the use of glass electrode. The experimental data were analyzed with the least-squares computer program SUPERQUAD to determine the complexes formed and their stability constants. In addition, the structure of the crystallized pyridine-2,6-carboxamidoxime complex with the formula [Ni(HL)2]4H2O has been determined with X-ray measurements.

The complexes of types Co(HL)2+ and Co(HL)22+ are mainly octahedral with a high spin $d^7$ electron structure ($t_{2g}^5e_g^2$) and their oxidation states are stable. The deprotonated bis complexes of type Co(HL)L+ are often low spin ($t_{2g}^5e_g$) and because of the easy loss of their only $e_g$ electron they are easily oxidized to very low spin cobalt(III) complexes ($t_{2g}^6$). Only small amounts of cobalt(III) complexes cause the very slow attainment of equilibrium often already in the pH range 2–5. Pyridine-2-carboxamidoxime and pyridine-2-aldoxime and probably also 1-(2-pyridinyl)ethanone oxime forms also tris complexes Co(HL)32+ and/or Co(HL)2L+.

The complex formation of pyridine-2-aldoxime in the pH range 5–10 could be studied by using very small cobalt(II) ion concentrations. There, all the cobalt(II) form the low spin CoL2, which quantitatively displaces also the tris complex Co(HL)2L+. 6-methylpyridine-2-aldoxime forms complexes Co(HL)2+, CoL+, CoL2, Co2L2OH+, Co2L3+, and Co2L3OH, mainly in the pH range 6–10. The stabilities of the low spin CoL2, Co2L3+, and Co2L3OH and their oxidation reactions are decreased by the steric requirements of the 6-methyl groups of the ligands.

Pyridine-2-acetamidoxime forms also a complex Co(H2L)3+ and pyridine-2-carboxamidoxime forms a complex Co2(HL)2H2L5+ with a positively charged ligand (H2L+).

Zinc(II) and cadmium(II) ions form with 6-methylpyridine-2-aldoxime only Zn2L22+, Zn2L2OH+, and Zn2L2OH2, and CdL+, CdL2, and Cd2L2OH+. With pyridine-2-acetamidoxime, they form only Zn(HL)2+, Zn2L2OH+, Cd(HL)22+, and CdL+. The other oximes form also Zn(HL)L+, ZnL2, Cd(HL)L+, and CdL2. Cd(HL)22+ reaches only with pyridine-2-carboxamidoxime and Zn(HL)22+ also with 1-(2-pyridinyl)ethanone oxime measurable concentrations. Pyridine-2-carboxamidoxime forms also Zn4(L–H)2L22+ and Cd4(L–H)2L22+.

The stability constants of the mono complexes M(HL)2+ increase with few exceptions in the order 6-methylpyridine-2-aldoxime < pyridine-2-acetamidoxime < pyridine-2-aldoxime < 1-(2-pyridinyl)ethanone oxime < pyridine-2-carboxamidoxime < pyridine-2,6-dicarboxamidoxime and Cd < Zn < Co < Ni < Cu.
The experimental work of this thesis was carried out in the Laboratory of Inorganic Chemistry at University of Helsinki.

I am most grateful to my supervisors Emeritus Professor Heikki Saarinen for the guidance at the beginning of the work and to Professor Timo Repo for the completion of the work.

I am also grateful for Doctors Helena Hyvönen, Marjatta Orama, and Pirkko Tilus for the obtaining advice in the processing of the titration results and use of the modern data processing programs. To Dr. Helena Hyvönen I am grateful also for the many advice in the final stages of the work.

Crystallization of the complexes formed was difficult. For only one complex was the crystal structure determined. For this, I am grateful to Dr. Ilpo Mutikainen.

However, the main difficulty of this work was the oxidation of the divalent cobalt ion in its deprotonated complexes to trivalent. One would think that deprotonation of the oxime group would shorten the bond between it and the metal ion. However, studies around the world show that this is certainly not the case. In the deprotonated bis-oxime complexes, the oxime and oximate groups are generally cis oriented forming an intramolecular hydrogen bridge. But deprotonation of their oxime group causes isomerization of the complex by trans orientation of the oximate groups due to the repulsive forces between the negatively charges. Also in the crystalline non-deprotonated bis-complexes, the oxime groups are (generally) trans oriented due to the repulsive forces between the oxime protons.

I wish to thank the reviewers of the manuscript, Professor Konstantin Popov and Professor Mika Sillanpää, for their valuable comments my work.

Helsinki, November 2020

Markku Salonen
LIST OF PUBLICATIONS


For publication I the author performed all experimental work and partly the processing of the results, designed the experimental work for cadmium (II) complexes, and wrote the manuscript.

For II, the author designed and performed all experimental work, the processing of the results, and wrote the manuscript.

For III, the author designed and performed the experimental work of the titrations in aqueous solution, the processing of the results, and wrote the manuscript.

For IV, the author designed and performed all experimental work, the processing of the results, and wrote the manuscript.

For V, the author wrote most of the text in the Results and Discussion section. Especially the interpretation of the results is the author’s output. “
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>3</td>
</tr>
<tr>
<td>Preface</td>
<td>4</td>
</tr>
<tr>
<td>List of original publications</td>
<td>5</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>7</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>8</td>
</tr>
<tr>
<td>2. Experimental</td>
<td>9</td>
</tr>
<tr>
<td>2.1. Reagents and solutions</td>
<td>9</td>
</tr>
<tr>
<td>2.2. Potentiometric measurements</td>
<td>10</td>
</tr>
<tr>
<td>2.3. Mathematical treatments of data</td>
<td>11</td>
</tr>
<tr>
<td>2.4. Evaluation of the equilibrium model</td>
<td>13</td>
</tr>
<tr>
<td>3. Results and discussion</td>
<td>15</td>
</tr>
<tr>
<td>3.1. Pyridine-2-aldoxime complexes</td>
<td>15</td>
</tr>
<tr>
<td>3.2. 6-methylpyridine-2-aldoxime complexes</td>
<td>34</td>
</tr>
<tr>
<td>3.3. 1-(2-pyridinyl)ethanone oxime complexes</td>
<td>43</td>
</tr>
<tr>
<td>3.4. Pyridine-2-carboxamidoxime complexes</td>
<td>51</td>
</tr>
<tr>
<td>3.5 Pyridine-2-amdioxime complexes</td>
<td>66</td>
</tr>
<tr>
<td>3.6. Pyridine-2,6-dicarboxamidoxime complexes</td>
<td>70</td>
</tr>
<tr>
<td>4. Summary and conclusions</td>
<td>80</td>
</tr>
<tr>
<td>References</td>
<td>85</td>
</tr>
</tbody>
</table>
ABBREVIATIONS

acac$^-$ acetylacetonate ion (acetylacetone = Hacac)

ao$^-$ 2-aminoamidoximate ion (2-aminoamidoxime = Hao)

ap$^-$ 3-aminopropanamidoximate ion (3-aminopropanamidoxime = Hap)

bipy 2,2$'$-bipyridine

$C_H$, $C_M$ and $C_L$ the total concentration of hydrogen ion, metal ion and ligand

dea$^-$ 2-(N-diethylamino)acetamidoximate ion

dma$^-$ 2-(N-dimethylamino)acetamidoximate ion

dmf dimethylformamide

dmg$^-$ dimethylglyoximate ion (dimethylglyoxime = Hdmg)

dmp$^-$ 3-(N-dimethylamino)propanamidoximate ion

emf electromotive force

en ethylenediamine

$h$ the concentration of the free hydrogen ion (= [H$^+$])

Hoad$^-$ oxamide dioximate ion (oxamide dioxime = H$_2$oad)

$I$ ionic strength

Im imidazole

M mol dm$^{-3}$

mM mmol dm$^{-3}$ (= $10^{-3}$ mol dm$^{-3}$)

ma$^-$ 2-(N-methylamino)acetamidoximate ion

Me methyl $-$CH$_3$ group

mp$^-$ 3-(N-methylamino)propanamidoximate ion

M$^z^+$ metal ion ($z$ = its charge number)

ox oxime or oximate group

Ph phenyl group

phen 1,10-phenanthroline

py pyridine

pz pyrazine

pza$^-$ pyrazine-2-carboxamidoximate ion (pyrazine-2-carboxamidoxime = Hpza)
1. INTRODUCTION

Equilibrium and structures of divalent copper, nickel, and zinc complexes with 2-aminoacetamidoxime,1–4 3-aminopropamidoxime5–8 and their methyl and ethyl derivatives of type RR’N(CH2)nC(NH2)NOH has been studied in our laboratory in the last decades. Following this, the studies has been continued on the following pyridine-2-oximes.9–13

![Pyridine-2-aldoxime](image1)
![6-methylpyridine-2-aldoxime](image2)
![1-(2-pyridinyl)ethanone oxime](image3)

In this work the studies has been expanded to the complexation of divalent cobalt, zinc, and cadmium ions with the five pyridine-2-oximes and to the complexation of pyridine-2,6-dicarboxamidoxime.

These pyridine oximes coordinate to the divalent metal ions mainly through their pyridine and oxime nitrogen atom forming five- or, in the case of pyridine-2-acetamidoxime, six-membered chelate rings. The complexes formed can polymerize through the oxime oxygen atoms and the amidoxime complexes also through the amido group in the form –NH–. The stability order of the most stable copper, nickel, zinc, and cadmium complexes of type M(HL)\(_n\)\(^{2+}\) with \(n = 1, 2\) or 3 is pyridine-2-carboxamidoxime > 1-(2-pyridinyl)ethanone oxime > pyridine-2-aldoxime.9–13 The stability of the pyridine-2-acetamidoxime complexes are weakened by their six-membered chelate rings. However, with divalent copper ion, the pyridine-2-acetamidoxime forms more stable complexes of Cu(HL)\(^{2+}\) and Cu(HL)\(^{2+}\) types than pyridine-2-aldoxime.9 It seems that the amide and methyl groups bonded to the oxime carbon atoms increase the stability of the complexes although they do not form any bond with the metal ion. The stability of the 6-methylpyridine-2-aldoxime complexes is deceased by the steric requirements of the 6-methyl group.10–13
The pyridine oximes are available reagents in analytical chemistry.\textsuperscript{14–19} Pyridine-2-aldoxime is also used to reactivate cholinesterase enzymes inhibited by organophosphorus compounds.\textsuperscript{20–22} The pyridine-2-aldoxime complexes CuL\textsubscript{2} and NiL\textsubscript{2} coordinate through two oximato bridges to alkaline earth metal 8-kinolates or 1-nitroso-2-naphtolates (MX\textsubscript{2}) to form inhibitors against some bacteria.\textsuperscript{22}

2. EXPERIMENTAL

2.1. Reagents and solutions

The water used was purified by a Millipore Milli-Q water purifier, which purifies the water by reverse osmosis, filtrations by active carbon, cation and anion exchange and filtration of the organic compounds. The resistivity of the purified water was generally ca. 18 MΩ cm.

The copper, nickel, cobalt, and cadmium chloride solutions were prepared by dissolving the weighted amounts of solid p.a. grade CuCl\textsubscript{2}, NiCl\textsubscript{2}, CoCl\textsubscript{2}, and CdCl\textsubscript{2} hydrates in the purified water. The zinc chloride solution was prepared by using solid p.a. grade ZnO, HCl Titrisol ampoule, and a volumetric flask of 500 ml (Emil, Green line). The metal ion contents of the stock solutions were standardized by EDTA titration. The copper(II) ion concentration was also determined electrogravimetrically and the nickel(II) ion concentration by precipitation with dimethylglyoxime.

The 0.100 M HCl and NaOH solutions used in the potentiometric titrations were prepared by using Titrisol ampoules (Merck) and volumetric flasks of 1000 ml (Emil, Green line). Their exact concentrations were standardized by potentiometric titration of the HCl solution with the NaOH solution. The acid contents of the metal chloride solutions were determined by titration with 0.1 M NaOH solution after liberation of the hydrogen ions by cation exchange.

Pyridine-2-aldoxime (99\% Aldrich, gold label) was taken to use without further purification. Pyridine-2-carboxamidoxime, pyridine-2-acetamidoxime, 1-(2-pyridinyl)ethanone oxime and 6-methylpyridine-2-aldoxime were prepared in our laboratory according to methods described in earlier papers.\textsuperscript{9,10} Pyridine-2,6-dicarboxamidoxime was synthetized 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.\textsuperscript{23} The white crystalline product was poorly soluble in water and common organic solvents. It was recrystallized form 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.
2.2. Potentiometric measurements

The investigation 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, the main salt in natural waters, was chosen as inert salt instead of the more common NaClO₄.

The titration system consisted of an autoburette (Metrohm Herisau Dosimat E 535), a magnetic stirrer (Metrohm Herisau E 649), a closed titration vessel and a digital potentiometer Radiometer PHM 52 connected to a sensitive REC61 servograph recorder. A water thermostat (B. Braun Melsungen AG, Thermomix 1430) to 25.0 ± 0.1 °C and nitrogen gas was passed through the solutions tempered in the titration vessel. The potentiometer was equipped to a Beckman glass electrode E 40495 and a calomel reference electrode with J-shaped liquid junction.

The free hydrogen concentration \( h \) was determined by measuring the emf of the cell:

\[
-Hg, Hg_2Cl_2 \parallel 0.10 \text{ M NaCl} \parallel \text{equilibrium solution} \parallel \text{glass electrode} +
\]

Assuming the activity coefficients to be constant, the emf \( E \) of the cell at 25.0 °C can be written as

\[
E = E_0 + 59.16 \log h + E_j
\]

(1)

The liquid junction potential \( E_j \) can be expressed as

\[
E_j = j_H h + j_{OH} K_w h^{-1},
\]

(2)

where \( j_H \) and \( j_{OH} \) are the liquid junction potential coefficients of the hydrogen and hydroxide ions and \( K_w \) is the ionic product of the water:

\[
K_w = [H^+][OH^-]
\]

(3)

According Näsänen \textit{et al.}\textsuperscript{24,25} the dependence of \( K_w \) on the ionic strength of NaClO₄ solution at 25.0 °C can be expressed as

\[
pK_w = 13.996 - 1.018l^{1/2}/(1 + 1.0l^{1/2}) + 0.26l,
\]

(4)

when the value of \( pK_w \) at zero ionic strength is taken to be 13.996.\textsuperscript{26} The calculated \( pK_w = 13.783 \) in 0.10 M NaClO₄ solution is in a good agreement with the experimental results \( pK_w = 13.775 \pm 0.001 \) in 0.1 M Na(Cl) solution at 25.0 °C determined by Sjöberg \textit{et al.}\textsuperscript{27} The difference between NaCl and NaClO₄ solutions increases in the increase of the ionic strength; for example, at 25 °C in 1 M NaCl and NaClO₄ solutions \( pK_w = 13.73 \) and 13.77, but it is, 14.03 and 14.17, respectively, in 3 M solutions.\textsuperscript{25}

\( E_0 \) and \( j_H \) were determined before each titration by adding exactly known 0.1 M HCl solution to 0.100 M NaCl solution. The observed \( j_H \) values were generally in agreement with the experimental
results, \( j_H = -511.5 \pm 4.9 \) and \( j_{OH} = 238.7 \pm 1.5 \text{ mV M}^{-1} \) in 0.1 M Na(Cl) solutions at 25.0 °C, and with the following equations:

\[
j_H = (-49.7 \pm 0.5)I^{-1} \text{ mV M}^{-1} \tag{5}
\]

\[
j_{OH} = (21.4 \pm 0.8)I^{-1} \text{ mV M}^{-1} \tag{6}
\]
determined in the ionic strength range \( I = 0.05\text{–}2 \text{ M Na(Cl)} \) at 25.0 °C by Sjöberg et al.\(^{27}\) In the pH range < 10 the term \( j_{OH}K_wI^{-1} \) of equation (2) is negligible (< 0.05 mV) in the relation to the accuracy of the potentiometer (±0.1 mV). In the higher pH range, it was possible to study only a few solutions. In the calculations the experimental \( j_{OH} = 238 \text{ mV M}^{-1} \) was used.

After the determination of \( E_0 \), the composition of the solutions was in general 50.00 ml 0.100 M NaCl + 7.00 ml 0.1 M HCl. Then, the necessary amounts of metal chloride solution and solid oxime was added to the acid solution and its initial pH was adjusted with the HCl solution. The solution prepared in this way was titrated with an exactly known 0.1 M NaOH solution. The available concentration and pH (= − log \( h \)) ranges were defined by the formation of a precipitate or very slow attainment of equilibrium.

2.3. Mathematical treatment of the data

In evaluating the equilibrium constants, the binary two-component equilibria (7–10) were considered:

\[
H^+ + HL \rightleftharpoons H_2L^+; \quad \beta_{101} \tag{7}
\]

\[
2H^+ + HL \rightleftharpoons H_3L^{2+}; \quad \beta_{201} \tag{8}
\]

\[
HL \rightleftharpoons H^+ + L^-; \quad \beta_{101} \tag{9}
\]

\[
pH^+ + qM^{2+} \rightleftharpoons (H^+)_{p}(M^{2+})_{q}; \quad \beta_{pq0} \tag{10}
\]

The acid strengths of the oxime –NOH groups are very weak, and thus the values of the corresponding \( p\beta_{101} \) (\( pK_a \)) values in reaction (9) are not very accurate. This is the reason to choose the ligand as a component in the form of the uncharged oxime (HL) in evaluating the stability constants of a three-component (\( H^+, M^{2+} \) and HL) system:

\[
pH^+ + qM^{2+} + rHL \rightleftharpoons (H^+)_{p}(M^{2+})_{q}(HL)_{r}; \quad \beta_{pqr} = \frac{[(H^+)_{p}(M^{2+})_{q}(HL)_{r}]}{[H^+]^p[M^{2+}]^q[HL]^r} \tag{11}
\]

In the evaluation of the three-component experimental data, the binary complex models were considered as known. The protonation constants of the ligands are given with the results of the
correspondent ligand. The binary hydrolytic equilibrium constants of cobalt(II), which were used (log $\beta_{-110} = -9.85$ and log $\beta_{-210} = -19.02$), were extrapolated from those determined in 0.25–3 M NaClO₄ solutions to ionic strength 0.1 M by Debye–Hückel-type equations established by Baes and Mesmer.²⁸ Similarly, the hydrolytic equilibrium constants of zinc(II) (log $\beta_{-110} = -9.15$ and log $\beta_{-210} = -8.89$) were extrapolated from those determined in 0.25–3 M NaClO₄ solutions to ionic strength 0.1 M by Debye–Hückel-type equations established by Baes and Mesmer.²⁸

Similarly, the hydrolytic equilibrium constants of cadmium(II) (log $\beta_{-110} = -10.01$ and log $\beta_{-110} = -11.8$) were calculated from that of $-11.6$ in KCl solution of $I = 0.1$ M at 30 °C determined by Chaberek et al.³² by using the hydrolytic enthalpy $\Delta H_{-110} = +54.8$ kJ mol⁻¹ determined by Arnek and Kakowicz.³³ The side reactions of the divalent metal ions of the first transition series with the chloride ion are smaller. For example, in NaClO₄ solution at $I = 1.0$ M the log $K_1$ values of CoCl⁺, NiCl⁺, and CuCl⁺, are 0.18, 0.16, and 0.13, respectively.³⁰,³⁴ The log $K_1$ value of ZnCl⁺ is 0.32 in fresh water ($I = 0.0015$ M), −0.25 in seawater ($I = 0.67$ M),³⁵ and −0.097 at $I = 1.0$ M.³⁰ It can be estimated to be about −0.1 at $I = 0.1$ M.³⁶ Because HCl is a very strong acid, it is completely in the form of Cl⁻ in the pH range 1–14. The coordination of the chloride ion to a metal ion does not affect the pH of the solution, so the glass electrode cannot distinguish chloro complexes from the free aqua ions or the mixed chloro oxime complexes from the oxime complexes. Thus, the possible chloro complexes have been ignored. The total concentrations of acid ($C_H$), metal ion ($C_M$) and ligand ($C_L$) are therefore:

$$C_H = 2[H_3L^{2+}] + [H_2L^+] - [L^-] + [H^+] - [OH^-] + \Sigma p[H^+]q(M^{2+})r(HL)_r = C_{HCl} - C_{NaOH}$$ (12)

$$C_M = [M^{2+}] + \Sigma q[H^+]p(M^{2+})q(HL)_r$$ (13)

$$C_L = [H_3L^{2+}] + [H_2L^+] + [HL] + [L^-] + \Sigma r[H^+]p(M^{2+})q(HL)_r$$ (14)

The mathematical analysis of data were performed with the least-squares computer program SUPERQUAD.³⁷ The program calculates the concentrations of the known and proposed species in every titration points by using equations (1)–(14). The $pqr$ triplets and corresponding equilibrium constants that best fit the experimental data were determined by minimizing the error sum:

$$U = \Sigma w_i(E_{i,obs} - E_{i,calc})^2$$ (15)

The weighting factor $w_i$ is determined by the equation

$$w_i = 1/(\sigma E^2 + \delta E/\delta V_i)\sigma v^2,$$ (16)
where $\sigma_E (= \pm 0.1 \text{ mV})$ and $\sigma_V (= \pm 0.02 \text{ ml})$ 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.

2.4. Evaluation of the equilibrium model

The SUPERQUAD program calculates $\chi^2$ and the sample standard deviation $s$ for every model, indicating the fit of the model with the experimental data.

The Bjerrum-plots,38,39 $Z_{HL}$ vs. log [HL], where $Z_{HL}$ denotes the ratio of the coordinated ligands to the total metal ion concentration, can be an aid in the evaluation. In the low pH ranges, most of the oxime complexes are in the form of $M(HL)_{r^2+}$. Then in the equation (12) the term $\Sigma p[(H^+)p(M^{2+})q(HL)_r] (= \Sigma p[M(HL)_{r^2+}]) = 0$ with $p = 0$, and according equation (14) $Z_{HL} = \Sigma r[M(HL)_{r^2+}]/C_M$. Reorganization of the contracted equation (12) gives:

$$2[H_3L_{2+}] + [H_2L^+] + [L^-] = C_{HCl} - C_{NaOH} - h + K_w h^{-1} \tag{17}$$

Substituting the concentrations $[H_3L_{2+}]$ and $[H_2L^+]$ calculated according the equations (7) and (8) and $[L^-] = 0$ to equation (17) gives:

$$[HL] = \frac{C_{HCl} - C_{NaOH} - h + K_w h^{-1}}{2\beta_201 h^2 + \beta_101 h} \tag{18}$$

and to equation (14) gives:

$$Z_{HL} = \frac{C_L - (\beta_201 h^2 + \beta_101 h + 1)[HL]}{C_M} \tag{19}$$

Assuming that only mononuclear complexes in the form $M(HL)_{r^2+}$ are present, the Bjerrum-plots $Z_{HL}$ vs. log [HL] coincide regardless of the concentrations $C_M$ and $C_L$ as well as of the ratio $C_L/C_M$. If deprotonated or polynuclear complexes are formed, the equation (17) is no longer valid ($p \neq 0$) and $Z_{HL}$ no longer indicates the average number of ligands HL ($= r$) in the complexes $(H^+)p(M^{2+})q(HL)_r$.* The $Z_{HL}$ curves are diverged.

If all the complexes are binary mononuclear of type $M_{L^2-r}$ ($p = -r$), the Bjerrum-plots and the total concentration of hydrogen ion ($C_H + C_L$) can be calculated over the zero level $L^-$, $M^{2+}$ and $H_2O$:

$$C_H + C_L = 3[H_3L_{2+}] + 2[H_2L^+] + [HL] + [H^+] - [OH^-] = C_{HCl} + C_L - C_{NaOH} \tag{20}$$

*This is the reason to replace the symbol $\bar{n}$, the average of $n$ for example in the complexes $M(HL)_{n^2+}$ (nHL) or $M_{n^2-r}$ ($\bar{n}$L), commonly used in the literature, with a different symbol $Z$ ($Z_{HL}$ or $Z_L$).
(CH has been calculated over the zero level HL, M\(^{2+}\), and H\(_2\)O). Substituting the equations

\[
[H_3L^2+] = \beta_{201}[H^+]^3[L^-]/\beta_{-101}, \quad [H_2L^+] = \beta_{101}[H^+]^2[L^-]/\beta_{-101} \quad \text{and} \quad [HL] = [H^+][L^-]/\beta_{-101}
\]  \hspace{1cm} (21)

to equations (20) and (14) gives [L\(^-\)] and

\[
[C_H] = \frac{[H_3L^2+] + [H_2L^+] + [HL]}{[H^+]^3 + [H_2L^+] + [H_3L^2+] + [HL]}
\]  \hspace{1cm} (22)

\[
Z_L = \frac{[L^-] - [H_2L^+] - 2[H_3L^2+] - \Sigma [H^+]_p(M^{2+})_q(HL)_r}{[L^-] + [HL] + [H_2L^+] + [H_3L^2+] + \Sigma [H^+]_p(M^{2+})_q(HL)_r}
\]  \hspace{1cm} (23)

\[
Z_H = \frac{[L^-] - [H_2L^+] - 2[H_3L^2+] - \Sigma [H^+]_p(M^{2+})_q(HL)_r}{[L^-] + [HL] + [H_2L^+] + [H_3L^2+] + \Sigma [H^+]_p(M^{2+})_q(HL)_r}
\]  \hspace{1cm} (24)

When [C\(_H\)] is calculated over the zero level HL, H\(_2\)O, and M\(^{2+}\) according the equations (12), (14) and (24):

\[
Z_H = \frac{[L^-] - [H_2L^+] - 2[H_3L^2+] - \Sigma [H^+]_p(M^{2+})_q(HL)_r}{[L^-] + [HL] + [H_2L^+] + [H_3L^2+] + \Sigma [H^+]_p(M^{2+})_q(HL)_r}
\]  \hspace{1cm} (25)

Also the Z\(_H\) values of the free ligand can be calculated according equation (25) by substituting \([H^+]_p(M^{2+})_q(HL)_r = 0\). Substituting \([H_3L^2+] = \beta_{201}[H][H^+]^2, [H_2L^+] = \beta_{101}[H][H^+]\quad \text{and} \quad [L^-] = \beta_{-101}[H][H^+]^{-1}\) calculated according the equations (8), (9) and (10) to equation (25) gives:

\[
Z_H = \frac{\beta_{-101}h - 2\beta_{201}h^2}{\beta_{-101}h^2 + \beta_{101}h + \beta_{201}h^2}
\]  \hspace{1cm} (26)

Thus, the Z\(_H\) curve of the free ligand vs. pH is independent on the total ligand concentration ([C\(_L\)]. It can be considered as a "bottom line" for the solutions, where the ligand forms complexes. When complexes are formed, the increase of the Z\(_H\) curves of the solutions in the increase of pH depends on the concentrations of the formed complexes according the equation (25). If the metal ion is in some pH range nearly completely as one complex \((H^+)_p(M^{2+})_q(HL)_r\), the Z\(_H\) curves of the solutions can have
plateau (slow increase) or an inflection point. If the plateau or the inflection point is in a pH range, where $h << -C_H >> K_{w}^{-1}$ ($C_H < 0$, when the HCl added to the solution is completely neutralized) and $[H_3L^2]$, $[H_2L^+]$ and $[L^-] \approx 0$, equations (12), (13) and (14) are contracted to the following forms:

\[ C_H = p[(H^+)q(M^{2+})r(HL)_c] \]  
\[ C_M = q[(H^+)q(M^{2+})r(HL)_c] \]  
\[ C_L = [HL] + r[(H^+)q(M^{2+})r(HL)_c] \]

In these conditions $[(H^+)q(M^{2+})r(HL)_c] = C_H/p = C_M/q$ and according to the $Z_H$ curves:

\[ p:q = C_H:C_M \text{ and } C_H = -Z_HC_L \]  

By means of the ratio $p:q$ the $pqr$ combination of the complex $(H^+)p(M^{2+})q(HL)_c$ can be estimated. For example, if $p:q = -3:2$, possible $pqr$ combinations are among other things $-322$, $-323$ and $-644$.

With the SUPERQUAD program the stability constants of the correspondent complexes can be estimated and the reliability of the given equilibrium model can be estimated by means of the $\chi^2$ and $s$ values.

3. RESULTS AND DISCUSSION

3.1. Pyridine-2-aldoxime complexes

At the end of the 1950s, pyridine-2-aldoxime was shown by Hartkamp\textsuperscript{14-16} to be a practical reagent in the spectrophotometric analytics of transition metals. In the following years, its complexation equilibria with transition metal ions interested many scientists.\textsuperscript{40-46} At the time, modern computer programs were unknown and the stepwise stability constants of the complexes $ML^r_{2-r}$ were red directly or by extrapolation in the Bjerrum plots $Z_L$ vs. $-\log [L^-]$ of the titrated solution. The complexes was generally supposed to be mainly of types $ML^+$, $ML_2$ and $ML_3^-$, so their stability constants ($\beta$, or $K_r$) were calculated conventionally over the zero level of hydrogen ions $L^-$, $H_2O$ and $M^{2+}$ according the equations:

\[ M^{2+} + rL^- \rightleftharpoons ML^r_{2-r}; \beta_r \]  
\[ ML^r_{2-r-1} + L^- \rightleftharpoons ML^r_{2-r}; K_r \]

However, in 1961, C. H. and C. F. Liu\textsuperscript{40} published the acidity constants of the complex $Cu(HL)_2^{2+}$ $pK_{a1} = 2.77$ and $pK_{a2} = 6.70$ in aqueous solution at 25 °C. In the following year, Kirson\textsuperscript{41} found that the copper(II) complexes polymerize in solutions, where $C_M = C_L$, in the pH range 5–8, so that the
complexation relieves 1.3–1.7 protons per copper(II) ion. By virtue of this observation he proposed the structure of the polymer to be \([\text{HL–Cu–O–Cu–L} \cdot 2\text{H}_2\text{O}]^+,\) where the ligands HL and L\(^-\) should be contacted by an intramolecular hydrogen bridge. It should decompose in the increase of pH to two complexes of CuL(OH)\(\cdot\)H\(_2\)O. At the same time, Hanania and Irvine\(^42\) determined the acidity constants of complex Fe(HL)\(_3\)\(^{2+}\) and the conventional stability constant of FeL\(_3^-\) (\(\beta_3\)) in many ionic strengths of 0.001–0.05 M NaCl and NaClO\(_4\) solutions at 17.5–33.5 \(\degree\)C with spectrophotometric studies.

The protonation of the pyridine ring is in pyridine-2-aldoxime (\(\log \beta_{101} = 3.56\) at low ionic strength\(^47\) and 3.590 in 0.1 M Na(Cl) solution\(^11\)) markedly weaker than in the unsubstituted pyridine (\(\log \beta_{101} = 5.25\) at 0 ionic strength\(^48\) and 5.33 \(\pm\) 0.01 in NaClO\(_4\) solution at 0.1 M ionic strength).\(^49\) This is due to the short distance of the electron-withdrawing oxime group from the pyridine ring. The oxime dissociation (p\(K_a = 10.17\)) is slightly stronger than in benzaldoxime (10.7) at low ionic strength.\(^50\)

In default modern data programs, the protonation of the complexes ML\(^+\), ML\(_2\) and ML\(_3^-\) was supposed generally to be insignificant and was ignored.\(^43\)–\(^45\) The polymerization of the complexes was prevented by using small metal ion concentrations and great ligand excesses.\(^45\),\(^46\) In our laboratory, these problems have been solved by the SUPERQUAD program. By means of this, the stability constants has been determined for pyridine-2-aldoxime complexes of the divalent nickel\(^10\) and copper.\(^11\) In this work the series has been continued to the divalent cobalt, zinc and cadmium ions. Series of solutions with different metal ion and ligand concentrations were titrated with an exactly known 0.1 M NaOH solution.

The cobalt(II) complexes are mainly octahedral, although the \(d^7\) electron structure favors high spin tetrahedral coordination with two fully occupied lower \(e\) and three half-occupied higher energy \(t_2\) orbitals (\(e^6t_2^2\)). The octahedral ligand field splitting (\(\Delta_o\)) is stronger than the tetrahedral one (\(\Delta_t = -4/9 \Delta_o\)). Therefore, the high spin cobalt(II) complexes are mainly octahedral complexes with \(t_{2g}^5e_g^2\) electron structure, but tetrahedral complexes are also known with several ligands. For example, in aqueous solution, there are always some tetrahedral aqua ions \([\text{Co(H}_2\text{O})_4]^{2+}\) in equilibrium with the octahedral high spin ones \([\text{Co(H}_2\text{O})_6]^{2+}\).\(^51\)

The octahedral cobalt(II) complexes have a low spin state (\(t_{2g}^5e_g\)) generally, when the energy level difference between \(t_{2g}\) and \(e_g\) orbitals is \(\Delta_o \geq 15\ 000\ \text{cm}^{-1} \ (\approx 180\ \text{kJ/mole}).\(^51\) Due to the uneven electron occupation in the \(e_g\) orbitals, the octahedral low spin cobalt(II) complexes are Jahn–Teller distorted. Because the only \(e_g\) electron is easily lose, the octahedral low spin cobalt(II) complexes are

\(^*\)Also Orama \textit{et al.}\(^11\) have noted that the complexation in a solution with \(C_M = C_L = 5\ \text{mM}\) relieves 1.3–1.7 (more accurately 1.33–1.67) protons per copper(II) ion in the pH range 5–8. SUPERQUAD calculations have indicated two trimers \(\text{Cu}_3\text{L}_3\text{OH}^{2+}\) and \(\text{Cu}_3\text{L}_3\text{O}^+\) (or \(\text{Cu}_3\text{L}_3(\text{OH})_2^+\)) instead of \([\text{HL–Cu–O–Cu–L} \cdot 2\text{H}_2\text{O}]^+\) and \(\text{CuL(OH)} \cdot \text{H}_2\text{O}\).
easily oxidized to the corresponding cobalt(III) complexes. Almost all the cobalt(III) complexes are octahedral with low spin state \((t_{2g}^6)\). Because both of their \(e_g\) orbitals are empty and all their \(t_{2g}\) orbitals are occupied, the cobalt(III) complexes are chemically very inert. Their ligand exchange reactions are very slow, and the attainments of equilibria usually take many months.

The increase of pH enhances the amount of low spin cobalt(II) complexes and the oxidation of the cobalt(II) complexes. The oxygen dissolved from the air to the reaction mixture probably act as oxidant. Although nitrogen gas was passed through the solution during all titrations, the complete elimination of oxygen should need a great excess pressure of nitrogen. During and after the NaOH addition, very high local concentrations of \(OH^-\) ion and low spin cobalt(II) complexes (CoL₂) can be formed a moment before the complete mixing of the solution. The low spin cobalt(II) complexes can also be oxidized by the oxygen molecules coming with the NaOH to the reaction mixture very quickly to cobalt(III) complexes (no nitrogen was passed through the NaOH solution). Overnight, the solutions could perhaps change a little to browner, but the yellow color was continued. The solutions left to evaporate, but only powder and NaCl crystals were precipitated. Attempts to crystallize complexes for X ray determination of their structures were unsuccessful.

Seven solutions with initial \(C_L = 4.86–8.64\) mM were titrated with 0.1 M NaOH using very strong nitrogen flow and strong magnetic mixing. Five solutions with initial \(C_M = 1.82–8.54\) mM could be titrated to pH 3.8–4.2, but two solutions with very low metal ion concentration \((C_M = 0.182–0.359\) mM) could be titrated to pH 10–11. The oxidation of low spin cobalt(II) complexes appeared to be strongest in the pH range 5–8, where only 0.02 ml titrant at a time could be added, but oxidation was not marked in the pH range 9–11.

In all solutions, the initial pink color weakened during the titration and gradually changed to an intense yellow. Hartkamp\(^{16}\) reported a similar observation in that solution of cobalt(II) obtain an intense yellow color. Bolton and Ellin\(^{44}\) have noted that the solutions are yellow in low pH ranges and yellow-orange in the high pH ranges. In this work, only the most dilute cobalt(II) solution \((C_M = 0.182\) mM and \(C_L = 5.68\) mM) became browner and more yellow-orange towards the end of titration. The yellow color returned at pH \(\approx 3\) by adding of 0.1 M HCl solution to samples of the solution. The other dilute cobalt(II) solution \((C_M = 0.359\) mM and \(C_L = 5.63\) mM) kept its yellow color until the end of the titration in the pH range 10–11. This solution was finally titrated by using the addition of only 0.02–0.05 ml NaOH in the pH range 5–8. In this way, the momentary great local \(OH^-\) ion concentrations and the oxidation of low spin cobalt(II) complexes were avoided where possible. Overnight, the solutions acquired a brownish tinge but the basic yellow color persisted.

The \(Z_H\) curves of only the two most dilute cobalt(II) solutions (Figure 1) exceed the zero level in the pH range 4–5, probing the formation of some deprotonated complexes. The complexations in
these solutions are best described by their $Z_L$ curves (Figure 2) over the zero level $L^-$, Co$^{2+}$ and H$_2$O. The $Z_L$ curve of the solution ($C_M = 0.359$ mM, $C_L = 5.63$ mM) hardly exceeds the value 2.0. Its decrease at the end of the titration points to hydrolysis or polymerization of some complexes. Also, Bolton and Ellin$^{44}$ and Burger et al.$^{45}$ have found that the $Z_L$ curves of the cobalt(II) solutions have the limiting value 2.0. Burger et al.$^{45}$ confirmed the composition of ML$_2$ for the cobalt(II), copper(II) and zinc(II) complexes from chloroform extracts with elemental analyses (C, H, N and metal). Electrophoretic measurements have shown that these complexes are uncharged but the formed iron(II) and nickel(II) complexes are negatively charged (ML$_3^-$)$^{45}$. The $Z_L$ curve of the most dilute cobalt(II) solution ($C_M = 0.182$ mM, $C_L = 5.68$ mM) at the end of titration is clearly higher than the latter curve, which can be due to the fact that a remarkable part of the cobalt(II) complexes should have been oxidized. Therefore, the curve of this solution is marked with a dashed line.

![Figure 1. Part of the experimental data plotted as $Z_H$ curves vs. pH for cobalt(II) complex formation with pyridine-2-aldoxime $HL$. The full lines have been calculated using sets of proposed stability constants in Table 1. The lowest line refers to the ligand alone.](image)

In the calculation of the stability constants of the complexes with the SUPERQUAD program, the pH range of the most dilute cobalt(II) solution was limited for the apparent oxidations under 5.6. The inaccuracies of the NaOH additions and the potential were assumed $\sigma_V = \pm 0.02$ ml and $\sigma_E = \pm 0.1$ mV. The pH range of the other dilute cobalt(II) solution was limited to 8.66, where the cobalt(II) ion was
already completely CoL₂. The SUPERQUAD program rejected the stability constants \( \beta_{-111}, \beta_{013}, \beta_{-213} \) and \( \beta_{-313} \) also by using wider pH ranges. No polynuclear complexes could be observed. The stability constants of \( \text{Co(HL)}^{2+}, \text{Co(HL)}_2^{2+}, \text{Co(HL)}L^+, \text{CoL}_2 \) and \( \text{Co(HL)}_2L^+ \) are given in Table 1 with the previously determined stability constants of another pyridine-2-aldoxime complexes. The distribution curves of two solutions are given in Figure 3. The computer program SPE⁵³ was used in these calculations.

\( \text{Co(HL)}_2L^+ \) appears in the pH range 3.0–3.5 (Figure 3), but its parent complex \( \text{Co(HL)}_3^{2+} \) never reaches measurable concentrations. This means for \( \text{Co(HL)}_3^{2+} \) \( pK_{a1} \leq 3.0–3.5 \) and \( \log \beta_{013} \leq 6.0–6.5 \). With the increase of pH \( \text{Co(HL)}_2L^+ \) is completely displaced by CoL₂ and the deprotonated complexes \( \text{Co(HL)L}_2 \) and \( \text{CoL}_3^- \) never reach measurable concentrations. Burger et al.⁴⁵ have proved with qualitative NMR measurements⁵⁴ that the pyridine-2-aldoxime complex CoL₂ is less paramagnetic than the aqua Co²⁺ ion, FeL₃⁻ is completely diamagnetic, and NiL₅⁻ is equally paramagnetic than the aqua Ni²⁺ ion in \( 10^{-2} \) M aqueous solution (at pH \( \approx 8 \)). The results show that CoL₂ and FeL₅⁻ are low spin but NiL₅⁻ is high spin and octahedral. Krause and Busch⁵⁵ prepared and characterized several solid nickel(II), palladium(II), and platinum(II) complexes with pyridine-2-aldoxime. All of the solid nickel(II) complexes, including \([\text{Ni(HL)}_3]_2\), \([\text{Ni(HL)}_2\text{Cl}_2]\), \([\text{Ni(HL)L}]\), and \([\text{NiL}_2]\), are paramagnetic with magnetic moments 3.01–3.56 BM. The palladium(II) and platinum(II) complexes \([\text{Pd(HL)L}]\text{Cl}\), \([\text{PdL}_2]\), and \([\text{PtL}_2]\) are square-planar and diamagnetic. \( \text{Pd(HL)}_2^{2+} \) is a strong diprotic acid.⁵⁵

![Figure 2](image-url)  
Figure 2. Part of the experimental data plotted as \( Z_{L} \) curves vs. \( \log [L^-] \) for cobalt(II) complex formation with pyridine-2-aldoximate ion \( L^- \) and the curve calculated according the stability constant \( \log \beta_2 = 15.1 \) of the complex CoL₂ (—).
Table 1. Proposed formulas and stability constants of pyridine-2-aldoxime complexes relating to reaction \( pH^+ + qM^{2+} + rHL \rightleftharpoons (H^+)p/M^{2+}q(HL)_r \) at 25°C.\(^a\)

<table>
<thead>
<tr>
<th>p</th>
<th>q</th>
<th>r</th>
<th>Proposed formula</th>
<th>M = Fe(^b)</th>
<th>M = Co (^b)</th>
<th>M = Ni (^c)</th>
<th>M = Cu</th>
<th>M = Zn</th>
<th>M = Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>M(HL)(^{2+})</td>
<td>2.85±0.02</td>
<td>4.19±0.02</td>
<td>3.93±0.09</td>
<td>1.90±0.02</td>
<td>2.02±0.02</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>M(HL)(^2+)</td>
<td>5.04±0.07</td>
<td>7.62±0.02</td>
<td>7.48±0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>3</td>
<td>M(HL)(^3+)</td>
<td>6</td>
<td>10.42±0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>ML(^+)</td>
<td>0.90±0.09</td>
<td>-4.81±0.29</td>
<td>-5.26±0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>M(HL)L(^+)</td>
<td>0.43±0.29</td>
<td>2.80±0.05</td>
<td>5.43±0.04</td>
<td>-2.50±0.24</td>
<td>-2.97±0.11</td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>1</td>
<td>2</td>
<td>ML(_2)</td>
<td>-4.92±0.23</td>
<td>-3.68±0.06</td>
<td>-1.53±0.04</td>
<td>-9.44±0.04</td>
<td>-10.93±0.03</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>3</td>
<td>M(HL)(_2)L(^+)</td>
<td>5.02</td>
<td>3.14±0.18</td>
<td>5.58±0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>1</td>
<td>3</td>
<td>M(HL)(_2)</td>
<td>1.57</td>
<td>-0.70±0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>1</td>
<td>3</td>
<td>ML(_3)</td>
<td>-5.45</td>
<td>-8.42±0.04</td>
<td>-17.09±0.18</td>
<td>-18.35±0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>2</td>
<td>2</td>
<td>M(_2)L(_2)(^{2+})</td>
<td>-6.76±0.27</td>
<td>-8.02±0.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>2</td>
<td>2</td>
<td>M(_2)L(_2)OH(^+)</td>
<td>-13.30±0.04</td>
<td>-16.66±0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td>2</td>
<td>2</td>
<td>M(_2)L(_2)(OH)(_2)</td>
<td>-22.66±0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td>3</td>
<td>3</td>
<td>M(_3)L(_3)OH(_2)</td>
<td>5.57±0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-5</td>
<td>3</td>
<td>3</td>
<td>M(_3)L(_3)O(^-) (or M(_3)L(_3)O(_3))</td>
<td>-0.97±0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Number of points/titrations: 297/7, 145/9, 360/12, 413/8, 465/8

\( \chi^2 \): 39.5, 47, 48.6, 53.3, 45.3

s: 1.59, 2.1, 2.75, 2.42, 1.89

Ref.: 30, II, 10, 11, I, I

\(^a\) In aqueous 0.1 M Na(Cl) solution unless advised to the contrary. The protonation and acidity constants of the ligand HL in the used solutions are given in Table 2.\(^b\) At ionic strength 0.045 M (NaCl or NaClO\(_4\)), where the conventional stability constant of FeL\(_3\)\(^-\), \( log \beta_3 = 24.85 ± 0.09 \) according to the equation (31), the acidity constant of the free ligand HL \( pK_{a1} = 10.10 \) and those of Fe(HL)\(_2\)\(^{2+}\), \( pK_{a1} ≈ 3.45 \) and \( pK_{a2} = 7.02 \). The listed stability constants were calculated according the following equations: \( log \beta_3 = log \beta_3 - 3pK_{a1} \), \( log \beta_2 = log \beta_3 + pK_{a3} \), \( log \beta_1 = log \beta_2 + pK_{a3} \) and \( log \beta_0 = log \beta_1 + pK_{a3} \). \(^c\) In aqueous 1.0 M Na(Cl) solution.

The octahedral low spin cobalt(II) complexes are Jahn–Teller distorted due to the uneven \( e_g \) electron occupation (\( t_{2g}^6 e_g \)). Therefore, in CoL\(_2\), both of the oximato ligands are located in the \( xy \) plane and the possible aqua ligands in the \( z \) axis. It is possible that CoL\(_2\) is at least partly square planar or square-pyramidal in aqueous solution. The comparable dimethylglyoxime complex Co(dmg)\(_2\) is square-planar in solid state, but is able to form halide and pseudohalide mixed complexes Co(Hdmg)(dmg)X\(_n\)\(^-\) (\( n = 1 \) or 2) with increasing acidity \( I^- < Br^- < Cl^- < SCN^- (pK_a ≈ 6.2) < Co(Hdmg)(dmg)^+ (pK_a ≈ 4.4) < SeCN^- \) in aqueous solution.\(^56,57\) Their stability constants calculated according the equation \( \beta_n = [Co(Hdmg)(dmg)X_n]\^{1-n}[Co(Hdmg)(dmg)]\(^-\)\([X^-]\)^n \) (without modern data programs) increase with increasing concentration of the present alkali metal ion and in the order...
Rb$^+$ < K$^+$ < Na$^+$ < Li$^+$, with reducing water activity ($a$). For example, the stability constant ($\log \beta_{2X}$) of Co(Hdmg)(dmg)Cl$_2$ is $0.12 \pm 0.04$ in RbCl solution ($a = 0.90$), $0.4 \pm 0.1$ in NaCl solution ($a = 0.885$), and $0.9 \pm 0.1$ in LiCl solution ($a = 0.86$). In potassium halide (KX) solution the stability of

Figure 3. Examples of the concentration distribution of cobalt(II) species with pyridine-2-aldoxime.
Table 2. Conventional stability constants\(^a\) of deprotonated pyridine-2-aldoxime complexes compared with \(\beta_{\text{011}}, \beta_{\text{012}}\) (see Table 1) and stepwise protonation constants\(^b\) of the ligand \(L^-\) in aqueous solution at 25 °C.

<table>
<thead>
<tr>
<th>(M^{2+})</th>
<th>(\log \beta_{\text{011}})</th>
<th>(\log \beta_{\text{012}})</th>
<th>(\log \beta_1)</th>
<th>(\log \beta_{\text{11}})</th>
<th>(\log \beta_{\text{2}})</th>
<th>(\log \beta_{\text{3}})</th>
<th>Medium(^d)</th>
<th>Method(^e)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>3.56</td>
<td>10.17</td>
<td>&lt;0.001 M</td>
<td>sp</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.52</td>
<td>10.10</td>
<td>0.045 M (NaCl(^f))</td>
<td>sp</td>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.590</td>
<td>10.01</td>
<td>0.1 M NaCl</td>
<td>gl</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>10.0</td>
<td>0.3 M NaClO(_4)</td>
<td>sp</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.865</td>
<td>9.922</td>
<td>1.0 M Na(Cl)</td>
<td>gl</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>5.2±0.2</td>
<td>9.1±0.2</td>
<td>0.3 M (NaClO(_4))</td>
<td>gl</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>8.4</td>
<td>16.1</td>
<td>21.2</td>
<td>&lt;0.01 M</td>
<td>gl</td>
<td>43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>17.4</td>
<td>22.5</td>
<td>0.1 M (KNO(_3))</td>
<td>gl(^f)</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>11.4</td>
<td>21.7</td>
<td>29.1</td>
<td>0.1 M (KNO(_3))</td>
<td>gl(^f)</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>2.85</td>
<td>5.04</td>
<td>10.44</td>
<td>15.1</td>
<td>0.1 M Na(Cl)</td>
<td>gl</td>
<td>II</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.8±0.1</td>
<td>17.6±0.1</td>
<td>0.3 M (NaClO(_4))</td>
<td>gl</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.6±0.2</td>
<td>17.2±0.2</td>
<td>0.3 M NaClO(_4)</td>
<td>sp</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>18.3</td>
<td>0.1 M (KNO(_3))</td>
<td>gl(^f)</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>4.19</td>
<td>7.62</td>
<td>12.72</td>
<td>16.16</td>
<td>21.35</td>
<td>1.0 M Na(Cl)</td>
<td>gl</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.4±0.2</td>
<td>16.5</td>
<td>22.0±0.4</td>
<td>0.3 M (NaClO(_4))</td>
<td>gl</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>14.2</td>
<td>21.2</td>
<td>0.1 M (KNO(_3))</td>
<td>gl(^f)</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(^{+})</td>
<td>11.05</td>
<td>14.4</td>
<td>14.48</td>
<td>?</td>
<td>pol(^b)</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.93</td>
<td>7.48</td>
<td>10.91</td>
<td>15.44</td>
<td>18.49</td>
<td>0.1 M Na(Cl)</td>
<td>gl</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>15.3</td>
<td>18.68</td>
<td>?</td>
<td>pol(^b)</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>15.85</td>
<td>18.6</td>
<td>0.5 M (NaNO(_3))</td>
<td>pol(^b)</td>
<td>46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.8</td>
<td>16.8</td>
<td>0.1 M (KNO(_3))</td>
<td>gl(^f)</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.9</td>
<td>14.55</td>
<td>&lt;0.02 M</td>
<td>gl</td>
<td>41</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>1.90</td>
<td>5.2±0.3</td>
<td>7.51</td>
<td>10.58</td>
<td>12.94</td>
<td>0.1 M Na(Cl)</td>
<td>gl</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.8±0.1</td>
<td>11.1±0.1</td>
<td>0.3 M NaClO(_4)</td>
<td>gl</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>10.8</td>
<td>0.1 M (KNO(_3))</td>
<td>gl(^f)</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>2.02</td>
<td>4.75</td>
<td>7.04</td>
<td>9.09</td>
<td>11.68</td>
<td>0.1 M Na(Cl)</td>
<td>gl</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>9.6</td>
<td>0.1 M (KNO(_3))</td>
<td>gl(^f)</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>6.5</td>
<td>12.2</td>
<td>0.1 M (KNO(_3))</td>
<td>gl(^f)</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) \(\log \beta_r = \log \beta_{\text{11}} + r \log \beta_{\text{11}2}\), where \(p\beta_{\text{11}2}\) is the acidity constant of \(LL^+ (=M^+H^+)\) in the correspondent medium. \(^b\) Indicated as stability constants of complexes \(HL\) (see footnote \(^a\)). \(^c\) The conventional stability constant of \(MHL^+ (=\log \beta_{\text{11}} + \log \beta_{\text{11}2})\). \(^d\) Or its ionic strength (the background electrolyte in parentheses). \(^e\) gl = glass electrode, sp = spectrophotometry, pol = polarography. \(^f\) Or NaClO\(_4\). \(^g\) At 24(±0.5) °C. \(^h\) The given log \(\beta_3\) has been determined polarographically in 0.2 M phosphate buffer solution at pH 12. \(^i\) At 20 °C. \(^j\) The acidity constants of \(HL\) (\(p\beta_{\text{11}2} = 10.04\)) and \(Cu(HL)^{2+}\) (\(p\beta_{\text{11}2} = 2.77\) and \(p\beta_{\text{112}} = 6.70\)) have been determined with glass electrode in dilute aqueous solution (\(\leq 0.01\) M CuCl\(_2\)). By using these values, the given log \(\beta_{\text{11}2}\) has been determined polarographically in 0.2 M phosphate buffer solution at pH 12. \(^k\) At 20 °C. \(^l\) The acidity constants of \(HL\) (\(p\beta_{\text{11}2} = 10.04\)) and \(Cu(HL)^{2+}\) (\(p\beta_{\text{11}2} = 2.77\) and \(p\beta_{\text{112}} = 6.70\)) have been determined with glass electrode in dilute aqueous solution (\(\leq 0.01\) M CuCl\(_2\)). By using these values, the given log \(\beta_{\text{11}2}\) has been determined polarographically in 0.2 M phosphate buffer solution at pH 12.
the mixed complexes increases in the order Cl\(^-\) < Br\(^-\) (log \(\beta_2^X\) = 0.60 ± 0.10) < I\(^-\) (4.0 ± 0.1) < SCN\(^-\) (7.8 ± 0.3) < Co(dmg)\(_2\)(SeCN)\(_2\)\(^2^-\) (8.0 ± 0.2). The size and the polarizability of the anions, the \(\pi\) acceptor capability of the ligands and the softness of the Lewis bases\(^{58}\) increase in the same order. Among the corresponding iron(II) complexes, the stability constants could be determined only for Fe(dmg)\(_2\)SCN\(^-\) (log \(\beta_1^X\) = 0.35 ± 0.05), Fe(dmg)\(_2\)(SCN)\(_2\)\(^2^-\) (log \(\beta_2^X\) = 1.30 ± 0.10), and Fe(dmg)\(_2\)(SeCN)\(_2\)\(^2^-\) (log \(\beta_2^X\) = 3.43 ± 0.07, \(K_2^X >> K_1^X\)). Qualitative NMR measurements\(^{54}\) indicate that Co(dmg)\(_2\), Fe(dmg)\(_2\), and all the mixed complexes are low spin in aqueous solution.\(^{56}\) The monohalide mixed complexes are softer Lewis acids and better \(\pi\) donors than Co(dmg)\(_2\) and Fe(dmg)\(_2\). For this reason, the stepwise stability order of the mixed complexes is reversed: \(K_1^X < K_2^X\), when \(K_1^X\) is small or the water activity is high. The decrease of the water activity in increasing background electrolyte concentration increases the stability of the monohalide mixed complexes in particular. For example, the stepwise stability constants of the mixed iodide cobalt(II) complexes Co(Hdmg)(dmg)I\(_n\)^\(-\)\(_n\) are in 1 M NaClO\(_4\) solution (\(a = 0.966\)) log \(K_1^X\) = 1.38 and log \(K_2^X\) = 1.98, in 4 M NaClO\(_4\) solution (\(a = 0.849\)) log \(K_1^X\) = log \(K_2^X\) = 2.40, and in 6 M NaClO\(_4\) solution (\(a = 0.763\)) log \(K_1^X\) = 3.86 and log \(K_2^X\) = 2.46.\(^{57}\) Apparently, the decrease of the water activity facilitates the dissociation of the aqua ligands and the coordination of a halide ligand to the \(z\) axis of Co(dmg)\(_2\). Jahn–Teller distortion weakens the stability of the dihalide mixed complexes. The coordination of a halide or SCN\(^-\) ion enhances the softness of the central ion as Lewis acid and leads to protonation of the mixed cobalt(II) complexes, because the uncharged dimethylglyoxime (Hdmg) is a softer Lewis base than the negatively charged dimethylglyoximate ion (dmg\(^-\)). The iron(II) ion is a clearly harder Lewis acid and the iron(II) mixed complexes are much less stable and not protonated.

The low spin iron(II) and cobalt(II) ions are markedly smaller (ionic radii 0.61 and 0.65 Å, respectively) than the high spin nickel(II) ion (0.690 Å).\(^{59}\) The smaller size of the metal ion strengthens the metal–ligand bonds, which weakens the O–H bonds in the oxime groups. Thus, the pyridine-2-aldoxime complexes Co(HL)\(_3\)^2\(^+\) (pKa\(_1\) ≤ 3.0–3.5), Fe(HL)\(_3\)^2\(^+\), Fe(HL)\(_2\)L\(^+\), and Fe(HL)L\(_2\) are much stronger acids than the corresponding nickel(II) complexes (Table 1). It is also clear that Co(HL)\(_2\)L\(^+\), Fe(HL)\(_2\)L\(^+\) and Fe(HL)L\(_2\) are low spin. Fe(HL)\(_3\)^2\(^+\) (log \(\beta_{013}\) ≈ 6), Co(HL)\(_3\)^2\(^+\) (≤ 6.0–6.5), and Ni(HL)\(_3\)^2\(^+\) (10.42) follow Irving–Williams\(^{60}\) stability order, and stepwise stability order of the cobalt(II) complexes is normal: \(K_1 > K_2 > K_3\). At least Co(HL)\(_2\)\(^+\), Co(HL)\(_2\)\(^2+\), Fe(HL)\(_2\)\(^+\), and Fe(HL)\(_2\)\(^2+\) are high spin. In Co(HL)\(_2\)\(^2+\), the low spin state is possible, if the Jahn–Teller distortion cancels the stability enhancement by spin pairing. The stability constants of the octahedral high spin iron(II) complexes (\(t_{2g}^4\) \(e_g^2\)) difficult to determine, because they are easily oxidized to octahedral high spin iron(III) complexes, where all the \(d\) orbitals are equally occupied (\(t_{2g}^3\) \(e_g^2\)).

The formation of zinc(II) complexes was possible to research with sufficient ligand excess in the pH range 9–10, but with low \(C_L:C_M\) ratios (≤ 1.1), a precipitate was formed already in the pH range
7.0–7.5. The ZH curves with \( C_L:C_M = 2–4 \) (Figure 4) revealed a weak inflection point at ca. \( C_H \approx -1.7 \ C_M \). Although this may suggest the presence of a trinuclear species with \( p:q = -5:3 \), such as \( \text{Zn}_3\text{L}_3\text{O}^+ \) or \( \text{Zn}_3\text{L}_3(\text{OH})_2^+ \), SUPERQUAD calculations led to much better \( \chi^2 \) and \( \sigma \) for a set of mono- and binuclear complexes \( \text{Zn}(\text{HL})^{2+}, \text{Zn}(\text{HL})\text{L}^+, \text{ZnL}_2, \text{Zn}_2\text{L}_2^{2+}, \text{Zn}_2\text{L}_2(\text{OH})^+, \) and \( \text{Zn}_2\text{L}_2(\text{OH})_2 \) than for any single tri- or tetranuclear species. The summation of \(-322\) and \(-212\) gives the same \( p:q \) ratio of \(-5:3\). The analysis, based on 413 titration points from eight titrations, terminated at \( \chi^2 = 53.3 \) and \( \sigma = 2.42 \). This can be considered to provide a fairly good explanation of the data (\( \sigma \) values lower than 3 are generally regarded as acceptable for comparable systems). The proposed complexes with their stability constants are given in Table 1. Distribution curves of the complexes are in Figure 5.

Zinc(II) ion has \( d^{10} \) electronic structure, which allows no ligand field stabilization energy. The complexes \( \text{Zn}(\text{HL})^{2+}, \text{Zn}(\text{HL})\text{L}^+, \) and \( \text{ZnL}_2 \) are clearly less stable than the corresponding cobalt(II) complexes. The aqua \( \text{Zn}^{2+} \) ion is precipitated in the pH range 7–8 as zinc hydroxide \( \text{Zn(OH)}_2 \). The \( pK_s \) value of the amorphous \( \text{Zn(OH)}_2 \) at 25 °C is in 0.2 M KNO\(_3\) and NaClO\(_4\) solutions 14.70 ± 0.03 and at zero ionic strength 15.52 ± 0.03.

Figure 4. Part of the experimental data plotted as \( Z_H \) curves vs. pH for zinc(II) complex formation with pyridine-2-aldoxime HL. The full lines have been calculated using sets of proposed stability constants in Table 1. The lowest line refers to the ligand alone.

Cadmium(II) hydroxide \( \text{Cd(OH)}_2 \) is more soluble than \( \text{Zn(OH)}_2 \) and allows titrating the solutions of low \( C_L:C_M \) ratios to pH range 8.0–8.5 and in the presence of twofold ligand excess to pH range 9–
The inflection points of the $Z_H$ curves (Figure 6) in the pH range 7–10 are clearly weaker than those of zinc(II) ion probing that the polymerization of cadmium(II) complexes is weaker than that of the zinc(II) complexes. Due to its larger ionic radius $^{59} (0.95 \text{ Å})$ and $d^{10}$ electronic structure, the cadmium(II) ion is clearly a soft Lewis acid, which more readily binds uncharged nitrogen donors through $\pi$-bonds than negatively charged oxygen donors through electrostatic forces. The smaller zinc(II) ion (ionic radius $^{59} 0.740 \text{ Å}$) has more properties of hard Lewis acids, more readily binding negatively charged ligands through electrostatic forces.

Figure 5. Examples of the concentration distribution of zinc(II) species with pyridine-2-aldoxime.
SUPERQUAD calculations show that Cd(HL)²⁺ (log β₀₁₁ = 2.02) is more stable than Zn(HL)²⁺ (1.90) but less stable than the other complexes of type M(HL)²⁺ formed by the metal ions of the first transition series (Table 2). The other cadmium(II) complexes are less stable and less acidic than the corresponding zinc(II) complexes (Table 1). Distribution curves of the cadmium(II) complexes are shown in Figure 7.

The stability constants calculated before the discovery of modern computer programs are listed in Table 2. These results are based to the supposition that pyridine-2-aldoxime should mainly form complexes according to equation (31). It is now known that the oximes form also complexes HₚM(HL)₂⁻ᵖ, where p ≠ −r. If such complexes are present in the solution, the equation (20) is no longer valid, and Zₗ does not give the average of r in the present complexes of types ML₂⁻ʳ.

![Figure 6](image-url)

Figure 6. Part of the experimental data plotted as Zₗ curves vs. pH for cadmium(II) complex formation with pyridine-2-aldoxime HL. The full lines have been calculated using sets of proposed stability constants in Table 1. The lowest line refers to the ligand alone.

The deprotonated mono complexes, ZnL⁺, CdL⁺, and CuL⁺ coordinate a free uncharged pyridine-2-aldoxime ligand HL according the following reaction

\[ \text{ML}^+ + \text{HL} \rightleftharpoons \text{M(HL)L}^+; \beta_{-112}/\beta_{-111} \]

(33) clearly more strongly than their parent aqua ions do (\(\beta_{-112}/\beta_{-111} > \beta_{011}\)). The formed complexes
M(HL)L⁺ are stabilized by intramolecular hydrogen bonding (=N–O–H⋯O–N=) between the cis oriented oxime and oximate oxygen atoms and the resultant extra chelate ring observed in many other similar compounds.¹,⁴,⁹,⁴⁰,⁶⁴–⁶⁶

C. F. and C. H. Liu⁶⁵ have observed both cis and trans oriented oximate groups in [PtL₂]·2H₂O. In 0.1 M HCl, cis-[PtL₂]·2H₂O dissolves instantly but trans-[PtL₂]·2H₂O only upon prolonged heating. Both of the dissolved cis and trans isomers can be isolated from the solution as bromide, chloride or

---

Figure 7. Examples of the concentration distribution of cadmium(II) species with pyridine-2-aldoxime.
PtCl₄²⁻ salts of only cis-Pt(HL)L⁺ and from the neutralized solution only as cis-[PtL₂]·2H₂O. From these results, it seems that the intramolecular hydrogen bonding and the extra chelate ring tend to stabilize the cis configuration of Pt(HL)L⁺ and serve to isomerize trans-[PtL₂]·2H₂O to cis through the formation of the intermediate cis-Pt(HL)L⁺. However, cis-[PtL₂]·2H₂O is converted to trans by heating at 140 °C or by heating in 1 M HCl followed by neutralization of the solution. The fact that the conversion of cis-[PtL₂]·2H₂O to trans requires more concentrated acid seems to indicate that both oximate groups may be protonated and that the resulting cis-Pt(HL)₂²⁺ loses the stabilizing influence of the extra chelate ring and rearranges to the trans configuration. The crystal structure of trans-[PtL₂]·2H₂O consists of linear chains of roughly square-planar PtL₂ units, which are hydrogen bonded through the oximate oxygen atom to water molecules.

In [PdL₂]·2H₂O only trans oriented oximate groups have been found. At room temperature, it dissolves instantly in 0.1 M HCl, from which it has been isolated as PdCl₄²⁻, Cl⁻, and NO₃⁻ salts of cis-Pd(HL)L⁺. From the neutralized solution cis-Pd(HL)L⁺ is isolated very quickly as trans-[PdL₂]·2H₂O. The palladium(II) complexes are labile and their isomerization and substitution reactions are rapid, but the platinum(II) complexes are inert and their isomerization and substitution reactions are very slow. For example, in aqueous solution at 25 °C, the first order water exchange constant kₑ of Pt(H₂O)₄²⁺ is 3.9·10⁻⁴ s⁻¹, but that of Pd(H₂O)₄²⁺ is 560 s⁻¹, and those of Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, and Cd²⁺ aqua ions are 10⁴–10¹⁰ s⁻¹. Also, these metal ions form labile complexes in aqueous solution.

In the crystalline [M(HL)₂(OOCC₃H₃)₂] complexes, where M = Ni, Zn, or Cd, the acetate ligands are monodentately coordinated in the angles: O─Ni─O 89.56°, O─Zn─O 92.39°, and O─Cd─O 95.55°. The oxime groups are trans oriented in the angles Nox─Ni─Nox 166.55°, Nox─Zn─Nox 158.75°, and Nox─Cd─Nox 155.72° forming intramolecular hydrogen bridges with their adjacent uncoordinated acetate oxygens N─O─H···OOCC₃. The H···O distance are 1.65–1.69 Å and the O···O distances are 2.463–2.545 Å.

In the crystalline Ni(HL)₂Cl₂, the oxime groups are trans oriented in the N─Ni─N angle of 171.73° and the pyridine nitrogens cis oriented in the N─Ni─N angle of 95.26°. The Cl─Ni─Cl angle is 92.83°. The oxime hydrogens form weak intramolecular hydrogen bridges with their adjacent chloride ligands (the H···Cl distances are 2.10 and 2.50 Å). The lengths of the Ni─NOH bonds are 2.039 and 2.048 Å. A similar structure in aqueous Ni(HL)₂(H₂O)₂²⁺ allows the formation of Ni(HL)₃²⁺ with mer oriented oxime groups. The crystalline octahedral tris complex Ni(HL)L₂·6½H₂O with mer oriented oxime and oximate groups is dimeric; the two parts of the molecule being together at the oxime ends by two hydrogen bridges N─O─H···O─N. The non-bridged N─O⁻ bonds (1.339 Å) are shorter than the bridged N─O⁻ bonds (1.354 Å), which are shorter than the N─OH bonds.
(1.380 Å). The deprotonation of the oxime group NOH of ligand HL to negatively charged oximate \( \text{NO}^- \) group shortens clearly the \( \text{N}--\text{O} \) bonds and would also increase the electrostatic attraction forces between the metal ion and the \( \text{NO}^- \) group. Despite this, both the bridged Ni--NO\(^-\) (2.100 Å) and the non-bridged Ni--NO\(^-\) bonds (2.077 Å) are longer than the Ni--NOH bonds (2.062 Å). The bridged and non-bridged Ni--NO\(^-\) bonds are \textit{trans} oriented at N--Ni--N angle of 170.9\(^\circ\),\(^\text{10}\) and the structural \textit{trans} effects\(^\text{75}\) of the oximate groups weaken (lengthen) the Ni--N bonds \textit{trans} to them. Apparently, the hydrogen bonding and protonation weaken the structural \textit{trans} effect of the --NO\(^-\) group. In aqueous solution, Ni(HL)\(_2\) is probably not dimeric and the oxime and oximate groups are hydrogen bonded with their adjacent water molecules. The Ni--N bonds are obviously not as long in the solution as in the solid state. The \textit{trans} effects of the ligands or their coordination groups are in solution kinetic and labilize the M--N bonds that are \textit{trans} to them. In octahedral complexes of divalent metal ions, the substitution reactions are generally dissociatively activated, and there is often a close correlation between the structural and kinetic \textit{trans} effects.\(^\text{75}\)

As in the crystalline Ni(HL)\(_2\)Cl\(_2\) the oxime groups are apparently \textit{trans} oriented also in the aqueous Ni(HL)\(_2\)(H\(_2\)O)\(_2\)\(^{2+}\) and Co(HL)\(_2\)(H\(_2\)O)\(_2\)\(^{2+}\). The dissociation of only one aqua ligand allows the rearrangements of HL ligands to a plane with \textit{cis} oriented oxime groups and the deprotonation of the complexes to Ni(HL)L\(^+\) and Co(HL)L\(^+\) in the pH range 3–6 (Figure 3) stabilized by the intramolecular hydrogen bonding O–H···O and the extra chelate ring. The about equal acidity constants of Co(HL)\(_2\)\(^{2+}\) (pK\(_{a1}\) = 4.61) and Ni(HL)\(_2\)\(^{2+}\) (4.82) calculated as stability differences \( \log (\beta_{012}/\beta_{-112}) \) prove that Co(HL)L\(^+\) is high spin. When \textit{cis}-Co(HL)L\(^+\) is deprotonated to \textit{cis}-CoL\(_2\), the repulsion forces between the adjacent negatively charged oximate oxygens very quickly cause its isomerization via tetrahedral CoL\(_2\) to square planar or octahedral low spin \textit{trans}-CoL\(_2\). The formation of CoL\(_2\) is also possible through deprotonation of \textit{trans}-Co(HL)\(_2\)\(^{2+}\) via \textit{trans}-Co(HL)L\(^+\) in the pH range 4–5, where CoL\(_2\) appears (Figure 3). The SUPERQUAD program is unable to distinguish between isomers of the same \( pq\) combination. It calculates for Co(HL)L\(^+\) only one stability constant according to equation (11) using the concentration [Co(HL)L\(^+\)] = \( \Sigma [\text{cis}-\text{Co(HL)L}\(^+\)] + \Sigma [\text{trans}-\text{Co(HL)L}\(^+\)] \). However, \textit{trans}-Co(HL)L\(^+\) is undoubtedly much less stable and a stronger acid than its \textit{cis} isomer and probably a stronger acid than its parent complex \textit{trans}-Co(HL)\(_2\)\(^{2+}\) (\( K_{a2} > K_{a1} \) or pK\(_{a2}\) < pK\(_{a1}\)), since they are both high spin but CoL\(_2\) is low spin. CoL\(^+\) and NiL\(^+\) have not been observed. Both Co(HL)\(^{2+}\) and Ni(HL)\(_2\)\(^{2+}\) disappear in the pH range 5.5–6.0 (Figure 3 and ref. 10). If their pK\(_{a}\) values are 6–7, CoL\(^+\) and NiL\(^+\) never reach measurable concentrations. Thus, the formations of Co(HL)L\(^+\) and Ni(HL)L\(^+\) according reaction (33) are very small.

The tetrahedral aqueous Co(HL)\(_2\)\(^{2+}\) is able to form Co(HL)\(_3\)\(^{2+}\) with both \textit{mer} and \textit{fac} oriented oxime groups. Co(HL)\(_3\)\(^{2+}\) deprotonates immediately to low spin Jahn–Teller distorted Co(HL)\(_2\)\(^{2+}\).
The intramolecular hydrogen bonding $\text{O} - \text{H} \cdots \text{O}^- \cdots \text{H} - \text{O}$ may be stronger between $\text{fac}$ oriented oxime and oximate groups than $\text{mer}$ oriented groups. The crystalline $[\text{Zn(HL)}_2\text{L}][\text{ZnI}_4]$ consists of two distorted octahedral $[\text{Zn(HL)}_2\text{L}]^+$ cationic parts and one distorted tetrahedral $[\text{ZnI}_4]^{2-}$ anionic part.\(^{76}\) In both of the cations, the oxime and oximate groups are $\text{fac}$ oriented forming intramolecular hydrogen bridges $\text{O} - \text{H} \cdots \text{O}^- \cdots \text{H} - \text{O}$. In one of the cations the $\text{H} \cdots \text{O}$ distances are 1.64 and 1.92 Å, and in the other 1.71 and 1.76 Å. The $\text{O}^- \cdots \text{O}$ distances are 2.535 and 2.556 Å in the former cation and 2.544 and 2.566 Å in the latter one.\(^{76}\)

![Figure 8](image-url)  
*Figure 8. Experimental data plotted as $Z_L$ curves vs. log $[\text{L}^-]$ for zinc(II) and cadmium(II) complex formation with pyridine-2-aldoximate ion $\text{L}^-$.***
The oximate groups are fac oriented also in the crystalline complexes [NiL3ML3Ni]ClO4, where the central M3+ ion (Mn3+ or Cr3+) is surrounded by six oximate oxygen atoms of the two fac-NiL3− units.77 Also in the polymeric \{(NiL3NaL3Ni)Na2OH(H2O)Py(H2O)2\}n, the central Na+ ion of each (NiL3)Na moiety is surrounded by six oximate oxygen atoms of the two fac-NiL3− units, but two oximato bridges of each NiL3− unit are branched to bind the two terminal Na+ ions.78 The (NiL3)Na moieties are linked together via the terminal Na+ centers by one aqua and one hydroxo ligand, resulting in a one-dimensional chain structure.78 The crystalline complex [Ni3(HL)L5]ClO4 consists of two NiL2 units and one Ni(HL)L unit. In only one of the NiL2 unit, the oximate groups are trans oriented and linked via oximato bridges to the other nickel(II) ions. In the other NiL2 unit and in the Ni(HL)L unit one oximate ligand forms branched bridges to the other nickel(II) ions completing their octahedral coordination spheres. The other oximate NO− and the NOH group are non-bridging and form an intramolecular hydrogen bridge (O—H···O). The Nox—Ni—Nox angles are 175.24, 109.94, and 108.32°.77 In [NiL2Py2]Py·3H2O crystallized from pyridine (Py) the pyridine ligands, oximate nitrogens, and the pyridine nitrogens of the ligands L− are mutually trans oriented with Py—Ni—Py, Nox—Ni—Nox, and Npy—Ni—Npy angles of 180.0°.78 The NiL2Py2 units are linked together through hydrogen bridges between the oximate oxygens and the lattice water molecules forming a hydrogen bonded one-dimensional chain structure.78 The coordinated pyridine ligand has no free electron pair to form hydrogen bridges.

The further deprotonation of Co(HL)2L+ to Co(HL)L2 causes repulsion forces between the adjacent oximate groups. If the oxime and oximate groups are mer oriented, the Jahn–Teller distorted Co—NOH bond is apparently not sufficiently strong on the z axis of Co(HL)L2. Thus, the ligand HL loses and the remaining CoL2 isomerizes so that both of the ligands L− are in the xy plane of CoL2 with trans oriented oximate groups.

Zn(HL)22+ does not reach measurable concentrations. The statistic ratios of the stepwise stability constants \(K_1:K_2:K_3\) of octahedral complexes for a bidentate ligand are 12:(5/2):(4/15).79 If both Zn(HL)22+ (log \(\beta_{011} = 1.90\) or \(\beta_{011} = 79.4\)) and Zn(HL)L2+ are octahedral, the stepwise stability constant of Zn(HL)22+ would be \(K_2 = 16.5\) or \(log K_2 = 1.22, log \beta_{012} = 3.12,\) and its \(pK_{a1} = 5.62.\) Apparently, the stability constants of Zn(HL)L2+ are smaller, and its cis isomers decompose at least partly due to the repulsion forces between the positively charged adjacent oxime protons. Thus, the proportion of Zn(HL)L2+ remains so small that it cannot be observed.

The stability constants of ZnL+ (log \(\beta_{−112} = −4.81 ± 0.29\)) and Zn(HL)L+ (log \(\beta_{−112} = −2.50 ± 0.24\)) are very inaccurate, because the complexes occur in the same pH range (Figure 5). However, it is reasonable to assume that the stepwise stability constant of Zn(HL)L+ log (\(\beta_{−112}/\beta_{−111}\)) = 2.3 ± 0.3 > log \(\beta_{011} = 1.90 ± 0.02,\) because Zn(HL)L+ is mainly formed via the coordination of HL to ZnL+ with
cis orientation of the oxime and oximate groups and stabilized by the intramolecular hydrogen bonding O–H⋯O. Its trans isomer is much less stable. If the stability constant of trans-Zn(HL)\(^{2+}\) \(\log \beta_{012} \approx 2.8\) \((K_2 \approx 8.3, \log K_3 \approx 0.9)\), and its acidity constants \(K_{a1} > K_{a2}\) \((pK_{a1} < pK_{a2})\) in its deprotonation via trans-Zn(HL)L\(^+\) to ZnL\(_2\) \((\log \beta_{-212} = -9.44)\), its pK\(_{a1}\) \(\leq 6.1\), pK\(_{a2}\) \(\geq 6.1\), and the stability constant of trans-Zn(HL)L\(^+\) would be \(\log \beta_{-112} \leq -3.3\). Thus, the proportion of trans-Zn(HL)L\(^+\) remains very small. It seems that the conventional stepwise stability constant of ZnL\(_2\) \(\log K_2 = 5.4 > \log K_1 = 5.2\) \((\pm 0.3)\).

The complex formation according to reactions (31) and (32) is very small in the pH range 5–9, where the free ligand is almost wholly in the form HL \((pK_a = 10.01)\). ZnL\(^+\) is formed through deprotonation of Zn(HL)\(^{2+}\) and ZnL\(_2\) mainly via coordination of HL to ZnL\(^+\) with trans orientation and following deprotonation of the formed trans-Zn(HL)L\(^+\). ZnL\(_2\) is also formed upon deprotonation of cis-Zn(HL)L\(^+\), but the repulsion forces between the negative charges of the adjacent oxime oxygens very quickly cause isomerization of the formed cis-ZnL\(_2\) to trans-ZnL\(_2\) and possibly its partial decomposition to ZnL\(^+\) and the free HL. CdL\(^+\), Cd(HL)L\(^+\), and CdL\(_2\) are formed in similar way than ZnL\(^+\), Zn(HL)L\(^+\), and ZnL\(_2\). However, the stepwise stability order of CdL\(^+\) and CdL\(_2\) is normal \(K_1 > K_2\). Apparently, trans-Cd(HL)L\(^+\) is only a slightly more potent acid than Cd(HL)\(^{2+}\) \((pK_a = 7.28)\).

The SUPERQUAD program calculates stability constants also for ZnL\(_3^-\) and CdL\(_3^-\) not observed earlier. The Z\(_L\) curves (Figure 8) with \(C_L:C_M = 3–4\) exceed the value of Z\(_L\) = 2.0 between the log \([L^-]\) values −3.5 and −3.0 showing the existence of ZnL\(_3^-\) and CdL\(_3^-\). The Z\(_L\) curve of zinc(II) ion published by Burger et al.\(^{45}\) ends at log \([L^-]\) \(\approx -3.5\) and it seems to reach the limiting value Z\(_L\) = 2.0 at log \([L^-]\) \(\approx -4.0\). The Z\(_L\) curves of zinc(II) and cadmium(II) ions published by Bolton and Ellin\(^{44}\) end already between the Z\(_L\) values 1.7–1.9, where the log \([L^-]\) values are between −5 and −4.

The distribution curves (Figures 5 and 7) show that both ZnL\(_3^-\) and CdL\(_3^-\) appear in the pH range 8.0–8.5. Apparently, they are also formed via the coordination of HL to ZnL\(_2\) and CdL\(_2\), respectively, and the coordination requires the oximate groups to be perpendicularly trans oriented in their parent complexes ZnL\(_2\) and CdL\(_2\). The formed Zn(HL)L\(_2\) and Cd(HL)L\(_2\) deprotonate without reaching measurable concentrations. Due to the repulsion forces between the mer oriented oximeters groups the conventional stepwise stability constants of ZnL\(_3^-\) \((\log K_3 = 2.36 \pm 0.22)\) and CdL\(_3^-\) \((2.59 \pm 0.16)\) are small. For the same reason, the stepwise stability constants of cis-ML\(_2\) complexes are also small. NiL\(_3^-\) \((\log K_3 = 5.19)\) is stabilized by the ligand field splitting, but cis-NiL\(_2\) probably isomerizes quickly to trans-NiL\(_2\). The detection of cis-[PtL\(_2\)]\(\cdot\)2H\(_2\)O is allowed only by its very slow isomerization.

In [Zn(HL)\(_2\)(OSMe\(_2\))\(_2\)][BF\(_4\)] crystallized from a mixture of dimethyl sulfoxide (Me\(_2\)SO), dimethylformamide (dmf), and methanol, the oxime groups are trans oriented in N\(_{ox}\)–Zn–N\(_{ox}\) angle of 158.75° and the O–Zn–O angle between the dimethyl sulfoxide ligands is 91.47°. The oxime
groups bind the [BF₄]⁻ anions with hydrogen bonds O−H⋯F. In [Zn(HL)₂(NCS)₂] crystallized from a mixture of methanol and dmf, the pyridine nitrogens are trans oriented in N−Zn−N angle of 162.1°. The Nox−Zn−Nox angle is 82.6° and the N−Zn−N angle between the thiocyanate ions is 94.7°. The intermolecular hydrogen bonds O−H⋯S between the oxime groups and the terminal sulfur atom of NCS⁻ link the complex molecules to form infinite layers.

Zn₂L₂²⁺ is probably formed by dimerization of ZnL⁺ via two oximato −NO⁻− bridges forming a six-membered (ZnNO)₂ ring. The dimer is deprotonated with pKₐ = 6.54 to Zn₂L₂OH⁺ by forming a hydroxo −OH⁻− bridge beside the (ZnNO)₂ ring. In the increase of pH, Zn₂L₂O⁻⁻ is further deprotonated to Zn₂L₂(OH)₂, but only one −OH⁻− bridge can exit at the same time between the zinc(II) atoms, if their coordination spheres are still octahedral. The bending of the (ZnNO)₂ ring breaks easily the hydroxo bridge and causes a collision of two adjacent aqua ligands on the opposite site of the broken hydroxo bridge. One of the two aqua ligands is then released as oxonium H₃O⁺ ion and the other deprotonated to OH⁻ ligand, which forms a new hydroxo bridge. Soon, the formed hydroxo bridge is broken and the former hydroxo ligand is again bridged. The two hydroxo ligands of Zn₂L₂(OH)₂ form alternatively short-lived hydroxo bridges between the zinc(II) atoms.

CdL⁺ dimerizes in a similar way to Cd₂L₂²⁺, which deprotonates with pKₐ = 8.64 to Cd₂L₂OH⁺ by forming a hydroxo bridge beside the (CdNO)₂ ring. Due to the larger size of cadmium(II) ion, Cd₂L₂²⁺ (log β⁻²²² = −8.02) and Cd₂L₂OH⁺ (log β⁻³²² = −16.66) are less stable and weaker acids than Zn₂L₂²⁺ (−6.76) and Zn₂L₂OH⁺ (−13.30, pKₐ = 9.36). Cd₂L₂(OH)₂ cannot be detected in the pH range 9–10.

The octahedral copper(II) complexes are Jahn–Teller distorted because of their t²g⁶e⁵g³ electron structure with three electrons in their two e⁵g orbitals. In the complexes Cu(HL)₂²⁺ and CuL₂, the ligands HL and L⁻ lie in the xy plane of the complex with trans oriented oxime and oximate groups. Jahn–Teller distortion prevents the coordination of the ligands HL or L⁻ on the z axis of Cu(HL)₂²⁺ and CuL₂, which is required for the formation of tris complexes with bidentate ligands.

Cu(HL)L⁺ is mainly formed via coordination of HL to CuL⁺ with cis orientation of the oxime and oximate groups and stabilized by the intramolecular hydrogen bonding O−H⋯O. Its stepwise stability constant log (β⁻₁₁₂/β⁻₁₁₁) = 4.53 > log β₀₁₁ = 3.93. Its trans isomer is much less stable. The stability constant of CuL₂ log β⁻₂₁₂ = −1.53. If the stepwise stability constant of trans-Cu(HL)L⁺ log (β⁻₁₁₂/β⁻₁₁₁) ≤ log (β₀₁₂/β₀₁₁) = 3.55, its stability and acidity constants are log β⁻₁₁₂ ≤ 4.45 and pKₐ ≤ 5.98. The acidity constant of its parent complex trans-Cu(HL)₂²⁺ (log β₀₁₂ = 7.48) is then pKₐ ≥ 3.03. The proportion of trans-Cu(HL)L⁺ remains small in solutions with Cₓₘ = 5 mM and Cₓₜ = 10 mM (Figure 2 in ref 11).

Instead of dimerization CuL⁺ trimerizes and hydrolyzes to Cu₃L₃OH²⁺ (pKₐ = 6.57) and Cu₃L₃O⁺ (or Cu₃L₃(OH)²⁺). The binuclear Cu₂L₂OH⁺ structure with octahedral coordination environments
would be highly unstable because of Jahn–Teller distortion. The trimers are main species at low CL:CM ratios (1:1) in the pH range 4–8, but in the presence of sufficient ligand excess (CL:CM ≥ 2) their proportions are small and the main species are Cu(HL)L+ and CuL2 in the pH range 3–9. The trinuclear Cu3O(H) core is held together by three peripheral oximato bridges.11,80 The oxygen atom in the core is located above the Cu3 plane and thus exhibits a roughly tetrahedral coordination sphere.80,81

The polymerization reactions require deprotonation of mono complexes in their oxime groups.

In the crystalline [CuL3CrT](ClO4)2, where T is 1,4,7-trimethyl-1,4,7-triazacyclononane, the coordination sphere around the Cu center is strongly distorted.82 The geometry of the Cu center may be envisaged as pseudo-trigonal-bipyramidal with a non-bonded pyridine nitrogen (at a distance of 2.490 Å from the Cu center, while the other Cu–N distances are 1.983–2.205 Å. In the crystalline [CuL3CrFeT](ClO4)2 the two oximate ligands deviate significantly from the z axis of the copper(II) ion: the Nox–Cu–Npy angle is 154.3°.83

It must be noted in Table 2 that the most stable bis complex formed by the uncharged pyridine-2-aldoxime is Cu(HL)2+ (log β012 = 11.05).46 The uncharged pyridine-2-aldoxime is a soft Lewis base and prefers to bind to the univalent copper ion, which is a much softer Lewis acid than for example divalent cadmium ion. Also, the negatively charged pyridine-2-aldoximate ion (L−) is a rather soft Lewis base; CuL2− (log β2 = 14.4) is more stable than ZnL2 (10.58) and CdL2 (9.09) but less stable than the ligand field stabilized CoL2, NiL2, and CuL2. It is generally very difficult to determine stability constants of copper(I) complexes, because they are easily oxidized by air oxygen.

3.2. 6-Methylpyridine-2-aldoxime complexes

In 1960, Hartkamp16 noted that 6-methylpyridine-2-aldoxime is a very selective reagent for spectrophotometric determinations of little amounts of copper (1–10 μg/ml) in presence of large excess of many another metals (for example in presence of 50 μg/ml Ni or 2500–5000 μg/ml Zn). 6-methylpyridine-2-aldoxime forms much less stable complexes with divalent transition metal ions than pyridine-2-aldoxime does, but both ligands form brownish orange copper(I) chelates with approximately equal intensity. The best pH range for the determination of copper with 6-methylpyridine-2-aldoxime is 4.5–6.5, where the formation of Cu(HL)2+ is complete. In the pH range 6.5–8.5, Cu(HL)2+ is deprotonated to Cu(HL)L and in the further increase of pH to CuL2−, which is also selective in alkaline solution (pH ≥ 12). These complexes are probably tetrahedral in aqueous solution, because copper(I) ion is a soft Lewis acid and water a hard Lewis base.61 All the copper(II) complexes formed by 6-methylpyridine-2-aldoxime are reduced rapidly to copper(I) complexes by
hydroxylamine also in cold solution. In the presence of air, the solutions of 6-methylpyridine-2-
aldoxime complexes Cu(HL)$_2^+$ and CuL$_2^-$ are stable at least 24 hours but all the copper(I) complexes
formed by pyridine-2-aldoxime, pyridine and 2-, 3- and 4-picoline are rapidly oxidized to
copper(II) complexes. It is clear that the 6-methyl groups give steric screenings from the air oxidation
of the central copper(I) ion in Cu(HL)$_2^+$, Cu(HL)L, and CuL$_2^-$ but weaken the stabilities of octahedral
complexes. A similar weakening effect of the 6- or 2-methyl groups on the complex stability has been
observed in comparable instances, with methylated pyridine and 2-picolinate ligands. With
large metal ions like Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Ag$^+$, and Hg$^{2+}$, the increased basicity of the ligand due to the
presence of methyl group may actually lead to the stabilization of the complexes. Such are the cases,
for example, with 6-methyl-2-picolinate ligand and with tetrahedral copper(I) complexes of 2-
picoline. Apparently, the 6-methylpyridine-2-aldoxime complexes Cu(HL)$_2^+$ and CuL$_2^-$ are
somewhat more stable than the corresponding pyridine-2-aldoxime complexes, although the stability
constants of last complexes (log $\beta$$_{1}$$ = 11.05$ and log $\beta$$_{2}$$ = 14.4$) in NaNO$_3$ solution ($I = 0.5$ M) at 20 °C
observed by Petitfaux are, according SPE calculation, also sufficiently large for the complete
complex formation in the pH ranges 4.5–6.5 and $\geq$ 12, respectively.

Orama et al. have determined the protonation and acidity constants of 6-methylpyridine-2-
aldoxime and the stability constants of its copper(II) and nickel(II) complexes in aqueous 0.1 M
Na(Cl) solution at 25 °C. In this work, the studies have been extended to its complex formation with
cobalt(II), zinc(II), and cadmium(II) ions.

The 6-methyl groups screen also the formed low spin cobalt(II) complexes from oxidation, but
the attainments of equilibria became slow already in the pH range 5–6, if the nitrogen current or the
magnetic mixing were insufficient. By using a sufficiently strong nitrogen current and magnetic
mixing, the titration could be continued to pH range 8–10. Then, the NaOH additions less than 0.1 ml
were not ever necessary in the pH range 5–8, as in the case of pyridine-2-aldoxime.

The pink color of the cobalt(II) ion disappeared in the solutions in the initial stages of the titrations,
and the solutions gradually developed a weak yellowish brown color. Hartkamp also observed the
same color after the addition of 6-methylpyridine-2-aldoxime to cobalt(II) salt solutions. In this work,
the color was strengthened in the pH range 6–8, and the solutions often had a reddish tone in the end
of the titrations (in the pH range 8–11). When the nitrogen current was stopped, the solutions
darkened fairly quickly and their pH values first raised something (contrary to the pyridine-2-
aldoxime complex solutions) but soon started again fall. The evaporations of also these solutions left
only powdery precipitate, which could not be used to determination of the structure of the complexes
with X-ray diffraction.

The dispersion of the $Z_H$ curves (Figure 9) is only weak in the pH range 4–6, where $Z_H \leq 0$,
indicating the stability constants of the complexes of the type Co(HL)$_r^{2+}$ are very small. The $Z_H$ curves
with \( \frac{C_L}{C_M} = 2-5 \) (Figure 9) have a plateau in the pH range 7−9 and an inflection point at \( C_H \approx -2C_M \) indicating that the major species should be \( \text{CoL}_2, \text{CoL}_2(OH)_2 \) or \( \text{CoL}_3\text{OH} \), where \( p = -2q \). The increases of the \( Z_H \) curves with low \( \frac{C_L}{C_M} \leq 1 \) over to level \( Z_H = 1 \) also indicates the existence of complexes, where \( p < -r \). The \( \text{SUPERQUAD} \) program calculated the stability constants for complexes \( \text{Co(}HL\text{)}^{2+}, \text{CoL}^+, \text{CoL}_2, \text{CoL}_2\text{OH}^+, \text{CoL}_3^+ \), and \( \text{CoL}_3\text{OH} \) but rejected the \( pqr \) combinations \(-012, -112, -312, -313, -222, -422, -433 \) and \(-533 \). The stability constants are given in Table 3. Examples of the distribution curves are given in Figure 10.

![Figure 9. Part of the experimental data plotted as \( Z_H \) curves vs. pH for cobalt(II) complex formation with 6-methylpyridine-2-aldoxime HL. The full lines have been calculated using sets of proposed stability constants in Table 3. The lowest line refers to the ligand alone.](image)

The conventional stability constants of \( \text{CoL}^- \) and \( \text{CoL}_2 \) are \( \log \beta_1 = 4.27 \) and \( \log \beta_2 = 10.11 \) (\( \log K_2 = 5.86 \)). The inverse stability order \( K_2 >> K_1 \) and the weak acidity of \( \text{Co(}HL\text{)}^{2+} \) (\( pK_a = 6.86 \)) prove that both \( \text{Co(}HL\text{)}^{2+} \) and \( \text{CoL}^+ \) are high spin but \( \text{CoL}_2 \) is low spin. Due to Jahn–Teller distortion, both of the ligands \( \text{L}^- \) would be expected to lie in the \( xy \) plane of \( \text{CoL}_2 \) with \textit{trans} oriented oximate groups. However, Kumar et al.\(^{87} \) have proved that 6-methylpyridine-2-aldoxime is a gravimetric reagent for the estimation of uranium(VI) ion as \( \text{UO}_2\text{L}_2 \), but unable to form any insoluble compound with palladium(II) ion. Uranium(VI) ion (0.73 Å) is sufficiently large\(^{59} \) to bind the two ligands \( \text{L}^- \) in the equatorial plane of the linear uranyl ion \( \text{UO}_2^{2+}. \)\(^{51} \) But palladium(II) ion, which almost invariably forms square-planar low spin complexes,\(^{51} \) is too small (0.64 Å) to bind two 6-methylpyridine-2-aldoximate ligands in its \( xy \) plane. The low spin cobalt(II) ion (0.65 Å) is also too small for their planar coordination. Only one of the ligands \( \text{L}^- \) may lie in the \( xy \) plane of \( \text{CoL}_2 \), but not both. If \( \text{CoL}_2 \) is octahedral and Jahn–Teller distorted, the uncharged \( \text{Co—N}_p \) bond is probably too weak to lie on its \( z \)
axis. The Co–NO\(^-\) bond is stronger to lie there, and the oximate groups are able to intramolecular hydrogen bonding with the aqua ligand of the \(xy\) plane (NO\(^-\)⋯H–O–H⋯ON). The intramolecular hydrogen bonding, along with the Jahn–Teller distortion, probably causes a significant deviation from the \(z\) axis of CoL\(_2\) for the Co–NO\(^-\) bond. Thus, CoL\(_2\) (log \(\beta_{212} = -9.77\)) is much less stable than NiL\(_2\) (\(-7.43\)).
Table 3. Proposed formulas and stability constants of 6-methylpyridine-2-aldoxime complexes relating to the reaction $p\text{H}^+ + q\text{M}^{2+} + r\text{HL} \rightleftharpoons (\text{H}^+)^p(\text{M}^{2+})^q(\text{HL})_r$ in aqueous 0.1 M Na(Cl) solution at 25 °C.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$q$</th>
<th>$r$</th>
<th>Proposed formula</th>
<th>$\log \beta_{pqr}$ $\pm 3\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>$\text{M(HL)}^{2+}$</td>
<td>$1.19 \pm 0.17$</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>$\text{M(HL)}_2^{2+}$</td>
<td>$3.86 \pm 0.04$</td>
</tr>
<tr>
<td>$-1$</td>
<td>1</td>
<td>1</td>
<td>$\text{ML}^+$</td>
<td>$-5.67 \pm 0.29$</td>
</tr>
<tr>
<td>$-1$</td>
<td>1</td>
<td>2</td>
<td>$\text{M(HL)L}^+$</td>
<td>$1.97 \pm 0.07$</td>
</tr>
<tr>
<td>$-2$</td>
<td>1</td>
<td>2</td>
<td>$\text{ML}_2$</td>
<td>$-9.77 \pm 0.09$</td>
</tr>
<tr>
<td>$-2$</td>
<td>2</td>
<td>2</td>
<td>$\text{M}_2\text{L}_2^{2+}$</td>
<td>$-8.24 \pm 0.24$</td>
</tr>
<tr>
<td>$-3$</td>
<td>2</td>
<td>2</td>
<td>$\text{M}_2\text{L}_2\text{OH}^+$</td>
<td>$-14.81 \pm 0.10$</td>
</tr>
<tr>
<td>$-4$</td>
<td>2</td>
<td>2</td>
<td>$\text{M}_2\text{L}_2(\text{OH})_2$</td>
<td>$-22.84 \pm 0.09$</td>
</tr>
<tr>
<td>$-3$</td>
<td>2</td>
<td>3</td>
<td>$\text{M}_2\text{L}_3^+$</td>
<td>$-11.47 \pm 0.09$</td>
</tr>
<tr>
<td>$-4$</td>
<td>2</td>
<td>3</td>
<td>$\text{M}_2\text{L}_3\text{OH}$</td>
<td>$-19.08 \pm 0.03$</td>
</tr>
<tr>
<td>$-4$</td>
<td>3</td>
<td>3</td>
<td>$\text{M}_3\text{L}_3\text{OH}^+$</td>
<td>$1.05 \pm 0.03$</td>
</tr>
<tr>
<td>$-5$</td>
<td>3</td>
<td>3</td>
<td>$\text{M}_3\text{L}_3(\text{OH})_2^+$</td>
<td>$-20.11 \pm 0.06$</td>
</tr>
</tbody>
</table>

Number of points/titrations: 227/5, 366/8, 306/8, 164/8, 253/8

$\chi^2$: 14.8, 20, 34.9, 53.6, 32.9

$s$: 1.84, 3.3, 2.27, 3.18, 2.72

Ref.: II, 12, 11, I, I

$^a$Calculated by using the following protonation and acidity constants of the free ligand HL: $\log \beta_{101} = 4.258 \pm 0.008$ and $\log \beta_{-101} = -9.94 \pm 0.08$ (ref. 11).

In Ni(\text{HL})^{2+}, the ligands HL are perpendicularly coordinated with $trans$ oriented oxime group. This is evidenced by the fact that the stepwise stability difference $\log (K_1:K_2)$ between Ni(\text{HL})^{2+} ($\log K_1 = 1.94$) and Ni(\text{HL})_2^{2+} ($\log K_2 = 1.92$) is only 0.02. The hydrophobic 6-methyl (─CH$_3$) groups expel water molecules from the coordination spheres of the complexes. This stabilizes the bis complexes by slowing their aquation reactions back to the mono complex. The structure of Ni(\text{HL})_2^{2+} with perpendicularly $trans$ oriented oximes remains the same when it deprotonates through Ni(\text{HL})L$^+$ to NiL$_2$. Apparently, the difference between the acidity constants of Ni(\text{HL})_2^{2+} ($K_{a1}$ and $K_{a2}$) is due to the intramolecular hydrogen bonding by the oximate oxygens with their adjacent aqua ligands in NiL$_2$ (NO$^-\cdot\cdot\cdot$H$_2$O$-$) so small that Ni(\text{HL})L$^+$ has not reached measurable concentrations (Table 3).$^{12}$

Also, the stability difference $\log (K_1:K_2)$ between Cu(\text{HL})^{2+} ($\log K_1 = 2.87$) and Cu(\text{HL})_2^{2+} ($\log K_2 = 2.42$) is smaller (0.45) than the statistic difference of octahedral mono and bis complexes for a bidentate ligand $\log (K_1:K_2) = \log (12.25) = 0.68$.$^{11,79}$ This and the acidity constants of Cu(\text{HL})_2^{2+}, $pK_{a1} = 3.32$, $pK_{a2} = 5.65$, which fit within the limits estimated above (p. 33) for the acidity constants of the corresponding pyridine-2-aldoxime complex $trans$-Cu(\text{HL})_2^{2+} ($pK_{a1} \geq 3.03$, $pK_{a2} \leq 5.98$),
indicate that the ligands HL/L$^-$ lie in the $xy$ planes of Cu(HL)$_2$$^{2+}$, Cu(HL)L$^+$, and CuL$^2$ with trans oriented oxime or oximate groups. The difference between the values of $pK_{a1}$ and $pK_{a2}$ is large, because the Jahn–Teller distortion hinders the intramolecular hydrogen bonding between the oximate groups and the aqua ligands. The steric requirements by the 6-methyl and oxime/oximate groups in the $xy$ plane diminish the stabilities of the bis complexes. Cu$_3$L$_3$OH$^{2+}$ is the main species in the pH range 4–7 also in the presence of twofold ligand excess.$^{11}$

In the binuclear complexes Co$_2$L$_3$$^+$ and Co$_2$L$_3$OH one of the cobalt(II) ions (in octahedral CoN$_4$O$_2$ or partly in square-pyramidal CoN$_4$O environment) is low spin and the other one surrounded by two nitrogen and four oxygen atoms (in CoN$_2$O$_4$ environment) is high spin. Co$_2$L$_3$$^+$ is probably formed through combination of CoL$_2$ and CoL$^+$ together via three oximato bridges with fac orientation to both cobalt(II) ions. Two of the oximato bridges bind the low spin cobalt(II) ion in its $xy$ plane and the third oximato bridge is Jahn–Teller distorted. The deprotonation Co$_2$L$_3$$^+$ to Co$_2$L$_3$OH in the pH range 7–9 requires the formation of a hydroxo $\text{OH}^-$ bridge and breaking of an oximato $\text{NO}^-\text{Co}$ bond, if the coordination spheres of the forming Co$_2$L$_3$OH are still octahedral. The Jahn–Teller distorted oximato bridge of Co$_2$L$_3$$^+$ is weak and easily broken; after bending of the remaining (CoNO)$_2$ ring, the hydroxo $\text{OH}^-$ bridge is formed on the opposite side of the opened oximato $\text{NO}^-$ group.

Co$_2$L$_2$OH$^+$ is apparently formed through dimerization of CoL$^+$ via two oximato bridges and deprotonation of the formed Co$_2$L$_2$$^{2+}$ ($pK_a < 7.0$) by forming a hydroxo bridge beside the (CoNO)$_2$ ring. Both of the cobalt(II) ions of Co$_2$L$_2$OH$^+$ are in CoN$_2$O$_4$ environments probably high spin. Due to the third Jahn–Teller distorted oximato bridge, Co$_2$L$_3$$^+$ ($pK_a = 7.61$) is a weaker acid than Co$_2$L$_2$$^{2+}$. The proportion of Co$_2$L$_2$OH$^+$ reaches about 20% of $C_M$ in solutions with $C_M \approx C_L$. In the presence of threefold ligand excess, Co$_2$L$_3$OH displaces CoL$_2$ as main species in the pH range 6–8 (Figure 10).

The structure of Ni$_2$L$_3$$^+$ is likely to be different to that of Co$_2$L$_3$$^+$, because one of the pyridine nitrogens can lie on the $z$ axis of the nickel(II) ion of the NiN$_4$O$_2$ environment. The perpendicularly trans oriented oximate groups allow NiL$_2$ to form insoluble polymers via oximato and hydroxo bridges starting with Ni$_3$L$_4$(OH)$_2$. In all solutions with $C_L \geq 1.5$ $C_M$, a precipitate or very slow attainment of equilibrium appears already in the pH range 6.5–7.5.$^{11}$ A light green crystalline complex [Ni$_9$L$_{10}$(OH)$_6$(H$_2$O)$_6$](ClO$_4$)$_2$·10H$_2$O has been isolated as perchlorate from solution, where $C_L = C_M$ and pH = 8.$^{12,88}$ This metallacrown$^{89}$ structure contains an octahedral NiO$_6$ central core, two NiL$_2$ units (two different NiN$_4$O$_2$ environments), and NiL units (two different NiN$_2$O$_4$ environments). Both of the NiL$_2$ units form with their adjacent NiL units two Ni$_3$L$_4$(OH)$_2$ units, where each nickel(II) atom is linked together via an oximato and a hydroxo bridge. The two Ni$_3$L$_4$(OH)$_2$ units are linked to the remaining nickel(II) atoms via several bi- or trifurcated oximato and hydroxo bridges.$^{12,88}$ In 0.1 M Na(Cl) solutions with $C_L \approx C_M$, the proportion of NiL$_2$ is so small that the titrations can be continued to pH range 8–9.$^{12}$ The main species is Ni$_2$L$_3$$^+$ (50–60% of $C_M$) in the pH range 6.0–7.5 and
Ni$_3$L$_3$(OH)$_2^+$ in the higher pH range.$^{12}$ Ni$_2$L$_3^+$ disappears in the pH range 8–9 without deprotonation to Ni$_2$L$_3$OH, although the proportion of Ni$_2$L$_3^+$ at pH = 8 is still about 20 % of $C_M$. Apparently, the nickel(II) ions of Ni$_2$L$_3^+$ are linked together via three oximato bridges with $fac$ orientation to both nickel(II) ions. If Ni$_2$L$_3^+$ is formed through combination of $trans$-NiL$_2$ to a mono complex, two oximato bridges are easily formed. The unbridged Ni$-$NO$^-$ bond is easily broken and after the following rotation of the ligand L$^-$ about 90° around its Ni$-$N$_{py}$ the third oximato bridge is formed.

It must be noted that also pyrazine-2-carboxamidoxime (Hpza) forms Co$_2$(pza)$_3^+$ ($\log \beta^{−323} = −13.53$) and Ni$_2$(pza)$_3^+$ ($−9.06$) in 0.1 M Na(Cl) solution.$^V$ Only Co$_2$(pza)$_3^+$ ($pK_a = 9.34$) is deprotonated to Co$_2$(pza)$_3$OH ($\log \beta^{−423} = −22.87$), but Ni$_2$(pza)$_3^+$ is displaced in the pH range 8–10 by Ni(Hpza)(pza)$_2$ ($\log \beta^{−213} = −6.02$) and Ni(pza)$_3^−$ ($\log \beta^{−313} = −16.12$). Ni$_2$(pza)$_3$OH is not formed, although the proportion of Ni$_2$(pza)$_3^+$ is about 55 % of $C_M$ at pH = 8 and still about 15 % at pH = 10 in solution of $C_M = 1$ mM and $C_L = 3$ mM. In Co$_2$(pza)$_3^+$ one of the cobalt(II) ions is low spin and the other is high spin. Thus, one of the three oximato bridges is Jahn–Teller distorted and easily broken, but all the three oximato bridges in Ni$_2$(pza)$_3^+$ are about equally strong. Co$_2$(pza)$_3^+$ ($pK_a = 9.34$) is a still weaker acid than the 6-methylpyridine-2-aldoxime complex Co$_2$L$_3^+$, but also the free pyrazine-2-carboxamidoxime Hpza ($pK_a = 11.17$) is a weaker acid than the free 6-methylpyridine-2-aldoxime HL (9.94). Thus, the basicity of the oximato $−NO^−$ group is stronger in the free pyrazine-2-carboxamidoximate pza$^-$ ion and the $−NO−Co$ (high spin) bond is stronger in Co$_2$(pza)$_3^+$ than in Co$_2$L$_3^+$.

The research of the zinc(II) complex formation to pH range 8–9 also required at least twofold ligand excess with this ligand. A weak infection point is observable on the titration curves at $C_H:C_M ≈ 1.85$ and pH ≈ 8.5–8.6. In the solution with low $C_L:C_M$ ratios ($≤ 1.1$) Zn(OH)$_2$ was precipitated in the pH range 7.0–7.5. The $Z_H$ curves of the solutions are close together before they exceed the zero level at pH range 6–7 (Figure 11). The SUPERQUAD program calculated stability constants only for Zn$_2$L$_2^{2+}$, Zn$_2$L$_2$OH$^+$, and Zn$_2$L$_2$(OH)$_2$ ($\chi^2 = 48.8$, $s = 3.13$; 171 data points form eight titrations). The sample standard deviation $s$ is somewhat high but still indicates a quite satisfactory explanation of the data. The mononuclear species Zn(HL)$_2^{2+}$ and Zn$^L$ never reach measurable concentrations, and the proportion of Zn$_2$L$_2^{2+}$ remains in all the solutions small (5–7 % of $C_M$). Zn$_2$L$_2$OH$^+$ is the major species in the pH range 7–8 (Figure 12). It is even more stable ($\log \beta^{−322} = −14.55 ± 0.04$) than Co$_2$L$_2$OH$^+$ ($−14.81 ± 0.10$). According the spectrochemical series of ligands, the $d$-orbital splitting increases in the order $I^- < Br^- < Cl^- < F^- < OH^- < C_2H_4^{2−}$ $≈$ H$_2$O $<$ NCS$^- <$ py $≈$ NH$_3 <$ en $<$ bipy $<$ phen $< NO_2^- <$ CN$^-$. $^{28,51,79}$ Water provides a relatively weak and hydroxide ion a slightly weaker ligand field. $^{28}$ As the deprotonation/hydrolysis of the aqua ion weakens the $d$-orbital splitting around the central metal ion, the acidity of the following aqua ions in aqueous solution decreases in the
strengthening of the ligand field in the order \( \text{Fe}^{2+} \) \((\log \beta_{\text{Fe}^{2+}} = -9.5 \text{ at } I \approx 0) > \text{Co}^{2+} \) \((-9.65) > \text{Ni}^{2+} \) \((-9.86) < \text{Zn}^{2+} \) \((-8.96). \) So \( \text{Co}_2\text{L}_2^{2+} \) is probably a weaker acid than \( \text{Zn}_2\text{L}_2^{2+} \) \((pK_a = 6.31). \) 

Figure 11. Part of the experimental data plotted as \( Z_H \) curves vs. pH for zinc(II) and cadmium(II) complex formation with 6-methylpyridine-2-aldoxime \( \text{HL} \). The full lines have been calculated using sets of proposed stability constants in Table 3. The lowest line refers to the ligand alone.

The formation of cadmium(II) complexes could be researched to pH range 8.0–8.5, and by using at least twofold ligand excess to pH range 9–10. On the titration curves in the pH range 8.8–9.3, a weak inflection point is observable at \( C_H:C_M = 1.69–1.86. \) This refers to complexes with \( p:r = 1.5 \) and
2, but the wide pH range proves that the latter complex ($p:r = 2$) is not formed through deprotonation of the former (1.5). The $Z_H$ curves (Figure 11) of the solutions exceed the zero level at somewhat higher pH range 6–7 than the $Z_H$ curves of the zinc(II) solutions. The SUPERQUAD program calculated stability constants only for CdL+, CdL2, and Cd$_2$L$_2$OH$^+$ ($\chi^2 = 32.9, s = 2.72; 263$ data points from eight titrations). Due to the large size of cadmium (II) ion, the polymerization of CdL$^+$ is weak. The proportion of Cd$_2$L$_2$OH$^+$ remains small (Figure 12) and CdL$_2$ is the main species in the pH range 8.5–10.0. The stepwise stability difference log ($K_1:K_2$) between CdL$^+$ (log $K_1 = 4.23$) and CdL$_2$ (log $K_2$)

Figure 12. Examples of the concentration distribution of zinc(II) and cadmium(II) species vs. pH with 6-methylpyridine-2-aldoxime solutions.
= 4.17, \( \log \beta_2 = 8.39 \) is 0.06, proving that also the oximate groups of CdL2 are perpendicularly trans oriented forming intramolecular hydrogen bridges with the adjacent aqua ligands (NO\(^{-} \cdots \cdot \cdot \cdot H_2O\)).

The complex formation of 6-methylpyridine-2-aldoxime in the pH range 4.5–6.5 is very weak with Zn\(^{2+} \) and Cd\(^{2+} \) ions (Figure 12) but not insignificant with Co\(^{2+} \) (Figure 10) and Ni\(^{2+} \) ions. The known copper concentration of 5.00 \( \mu \)g/ml determined at pH = 5 as Cu(HL)\(^{2+} \) gives 4.95 \( \mu \)g/ml Cu in the presence of 5000 \( \mu \)g/ml Zn\(^{2+} \) or 1000 \( \mu \)g/ml Cd\(^{2+} \). The same copper concentration gives 5.26 \( \mu \)g/ml Cu in the presence of 50 \( \mu \)g/ml Co\(^{2+} \) and 5.20 \( \mu \)g/ml Cu in the presence of 500 \( \mu \)g/ml Ni\(^{2+} \), if the solution contains tartaric acid 5 mg/ml. For the determination of copper in alloys of aluminum, zinc, antimony or tin, the measurement in alkaline appears advantageous. The known copper concentration of 5.00 \( \mu \)g/ml determined at pH = 12 as gives CuL\(^{-} \) gives exactly 5.00 \( \mu \)g/ml Cu in the presence of 2500 \( \mu \)g/ml Zn\(^{2+} \). This proves that ZnL\(_2\)(OH)\(_2\) hydrolyzes completely in very alkaline solution but CuL\(_2\) is stable still at pH = 12.

3.3. 1-(2-Pyridinyl)ethanone oxime complexes

1-(2-pyridinyl)ethanone oxime is a derivative of pyridine-2-aldoxime, where the aldoxime hydrogen is replaced by a methyl \(-\text{CH}_3\) group. It is also a derivative of acetaldoxime (predicted p\(K_a\) = 11.82 \( \pm \) 0.10), where the aldoxime hydrogen is replaced by pyridine ring. It belongs to ketoximes. Other derivatives of acetaldoxime are acetophenone oxime (p\(K_a\) = 11.48), where the aldoxime hydrogen is replaced by a benzene ring, and acetoxime (at 24.9 °C p\(K_a\) = 12.42 at \( I = 0 \) and 12.20 at \( I = 0.10 \) M).

The electron-withdrawing pyridine and benzene rings decrease but the additional methyl group in acetoxime increases the electron density on the oxime group. Thus, the oxime dissociation is stronger in 1-(2-pyridinyl)ethanone oxime (p\(K_a\) = 10.87 in 0.1 M Na(Cl) solution) than in acetaldoxime but weaker than in pyridine-2-aldoxime (10.00). The increased electron density strengthens the NO–H bond and in the protonated ligand H\(_2\)L\(^{+} \) also the heterocyclic N–H\(^{+} \) bond. So the protonation is in 1-(2-pyridinyl)ethanone oxime (log \( \beta_{101} \) = 3.968) is stronger than in pyridine-2-aldoxime (3.590).

The complex formation equilibria of 1-(2-pyridinyl)ethanone oxime with divalent copper and nickel ions in aqueous 0.1 M Na(Cl) solution at 25 °C have been studied earlier. In this work, the studied were continued to cobalt(II), zinc(II), and cadmium(II) ions.

In all the solutions, the pink color of the cobalt(II) ion changed with the first addition of NaOH, making the solutions yellowish or brownish. During titration, the solutions darkened to yellow-brown, and the attainments of equilibria became slow already in the pH range 2.7–2.9. This indicates the formation of low spin cobalt(II) complexes in such low pH ranges in the solutions and their at least
partial oxidation to cobalt(III) complexes. The dispersion of the $Z_H$ curves (Figure 13) indicates that the complex formation should be strong already in the pH range 1.7–2.0. The low and narrow pH range is very unfavorable for determination of stability constants. The SUPERQUAD program calculated among the five complexes $\text{Co(HL)}^{2+}$, $\text{Co(HL)}_2^{2+}$, $\text{Co(HL)}_3^{2+}$, $\text{Co(HL)L}^+$ and $\text{Co(HL)}_2L^+$ the stability constants generally only for the complexes $\text{Co(HL)}^{2+}$, $\text{Co(HL)}_2^{2+}$ and $\text{Co(HL)L}^+$. This model is very unreliable because of the unusual stepwise stability order: $K_3 > K_1 > K_2$. Although the tris complex $\text{Co(HL)}_3^{2+}$ were low spin, its stability should be weakened by Jahn–Teller distortion. It is also very improbable that the smaller-sized low spin tris complex $\text{Co(HL)}_3^{2+}$ were a weaker acid by 2–3 log units than the high spin bis complex $\text{Co(HL)}_2^{2+}$. Removing $\text{Co(HL)}_3^{2+}$ led to further rejection of $\text{Co(HL)}_2L^+$ and to calculation of the stability constants of the complexes $\text{Co(HL)}^{2+}$, $\text{Co(HL)}_2^{2+}$ and $\text{Co(HL)L}^+$. The lowest limits of the pH ranges of the solutions could be set to 1.80, because the $Z_H$ curves (Figure 13) of the solutions increases regularly. In this way, the program calculated the stability constant given in Table 4 with $\chi^2 = 12.58$ and $s = 2.94$. The sample standard deviation $s$ is somewhat large, because of the low and narrow pH range, but still indicates a satisfactory explanation of the data. An example of the concentration distribution of the species is given in Figure 14.

![Figure 13](image_url)

**Figure 13.** Part of the experimental data plotted as $Z_H$ curves vs. pH for cobalt(II) complex formation with 1-(2-pyridinyl)ethanone oxime HL. The full lines have been calculated using sets of proposed stability constants in Table 4. The lowest line refers to the ligand alone.
Table 4. Proposed formulas and stability constants\(^a\) of 1-(2-pyridinyl)ethanone oxime complexes relating to the reaction \(pH^+ + qM^{2+} + rHL \rightleftharpoons (H^+)_p(M^{2+})_q(HL)_r\) in aqueous 0.1 M Na(Cl) solution at 25 °C.

<table>
<thead>
<tr>
<th>(p)</th>
<th>(q)</th>
<th>(r)</th>
<th>Proposed formula</th>
<th>(\log \beta_{pqr}\pm3\sigma)</th>
<th>(\chi^2)</th>
<th>(s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>M(HL)(^{2+})</td>
<td>3.74(\pm)0.09</td>
<td>10.7</td>
<td>2.93</td>
<td>II</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>M(HL)(^{2+})</td>
<td>7.0 (\pm)0.3</td>
<td>35</td>
<td>2.1</td>
<td>12</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>3</td>
<td>M(HL)(^{2+})</td>
<td>12.88(\pm)0.04</td>
<td>34.6</td>
<td>2.90</td>
<td>11</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>ML(^{+})</td>
<td></td>
<td></td>
<td>2.93</td>
<td>1</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>M(HL)L(^{+})</td>
<td>4.25(\pm)0.15</td>
<td></td>
<td>2.1</td>
<td>1</td>
</tr>
<tr>
<td>-2</td>
<td>1</td>
<td>2</td>
<td>ML(_2)</td>
<td>-3.55(\pm)0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>1</td>
<td>1</td>
<td>M(HL)(_2)L(^{+})</td>
<td>7.28(\pm)0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>1</td>
<td>2</td>
<td>M(HL)L(_2)</td>
<td>-0.09(\pm)0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>2</td>
<td>3</td>
<td>M(_2)L(^{3+})</td>
<td>-9.31(\pm)0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2</td>
<td>2</td>
<td>2</td>
<td>M(_3)L(^{2+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>2</td>
<td>2</td>
<td>M(_3)L(_2)OH(^+)</td>
<td>-12.72(\pm)0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td>2</td>
<td>2</td>
<td>M(_3)L(_2)(OH)(_2)</td>
<td>-20.70(\pm)0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>2</td>
<td>3</td>
<td>M(_3)L(^{4+})</td>
<td>-1.33(\pm)0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td>3</td>
<td>3</td>
<td>M(_3)L(_3)OH(^2+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-5</td>
<td>3</td>
<td>3</td>
<td>M(_3)L(_3)O(^+) (or M(_3)L(_3)(OH)(_2)(^+))</td>
<td>3.47(\pm)0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Number of points/titrations: 129/6, 433/8, 450/12, 425/8, 458/8

\(\chi^2\): 10.7, 35, 34.6, 25.2, 32.6

\(s\): 2.93, 2.1, 2.90, 2.1, 2.33

Ref.: II, 12, 11, 1

\(^a\) Calculated by using the following protonation and acidity constants of the free ligand HL: \(\log \beta_{101} = 3.968 (\pm0.003)\) and \(\log \beta_{101} = -10.87 (\pm0.03)\) (ref. 11).

Co(HL)\(^{2+}\) and Co(HL)\(^{2+}\) are less stable than Ni(HL)\(^{2+}\) and Ni(HL)\(^{2+}\) (Table 4). This and the normal stepwise stability order \(\log K_1 = 3.74 < \log K_2 \approx 3.3\) prove that both of the cobalt(II) complexes are high spin. But the formation of Co(HL)L\(^{+}\) already in the pH range 2.0─2.1 proves that it is low spin unlike the corresponding pyridine-2-aldoxime complex. The replacing of the aldoxime hydrogen atom by a methyl group strengthens the ligand field around the metal ion and the stability of the complex. In the crystalline distorted square-pyramidal \([Cu(HL)LCl] \cdot 3H_2O\) the N─O\(^-\) bond (1.333 Å) is shorter than the N─OH bond (1.359 Å), but the Cu─NO\(^-\) bond (2.004 Å) is longer than the Cu─NOH bond (1.975 Å).\(^93\) In the deep orange octahedral \([Ni(HL)L(H_2O)_2]NO_3\), the N─O\(^-\) bond (1.362 Å) is shorter than the N─OH bond (1.381 Å) and also the Ni─NO\(^-\) bond (2.031 Å) is shorter than the Ni─NOH bond (2.042 Å).\(^94\) An intramolecular hydrogen bridge exists between the \(cis\) oriented oxime and oximate groups (O─H∙∙∙O) in both of the crystalline complexes\(^93,94\) and
undoubtedly also in the aqueous Co(HL)L⁺. The Ni─NOH distances are 2.039 Å in the crystalline Ni(HL)₂Cl₂, 1 Å in Ni(HL)₂Br₂, 2.059 Å in Ni(HL)₂(NO₃)₂, and 2.0670 Å in [Ni(HL)₂(OOCPh)₂]. All four complexes are slightly distorted octahedral with trans oriented oxime groups at N─Ni─N angles of 165−170° and cis oriented monodentate ligands at angles of 85−94°. Their crystal structures show intramolecular hydrogen bonding between the oxime hydrogen and their adjacent bound anion or the uncoordinated oxygen atom of the monodentate nitrate ─ONO₂ and phenolate ─OOCPh ligands. The NOH···Cl distances are 2.23 and 2.24 Å, the NOH···Br distances are 2.36 and 2.50 Å, the NOH···ONO₂ distances are 1.88 Å (O···O distances 2.677 and 2.686 Å), and the NOH···OOCPh (O···O) distances are 1.58 (2.4848) and 1.616 (2.5190) Å. In the crystalline [Ni(HL)₃](NO₃)₂·½H₂O the oxime groups are mer oriented, the Ni─NOH distances are 2.0631−2.0866 Å, and the oxime hydrogen atoms form hydrogen bonds to the free nitrate anions. Co(HL)₂⁺ and Co(HL)₂L⁺ have probably a similar structure, but they do not reach measurable concentrations in the pH range 2.5−2.9. This is not possible, if log β₀₁₃ = 9.0−9.5 (log K₃ = 2.0−2.5) and log β⁻¹₁₃ ≤ 6.0. At least Co(HL)₂L⁺ would be low spin and Jahn–Teller distorted.

The zinc(II) solutions were in the presence of sufficient ligand excess still stable in the pH range 9−10. The ZH curves (Figure 15) show complex formation already in the pH range 2−3. A weak inflection point appeared at C₇H:C₇M = −1 in the titration curves of solutions with C₇L:C₇M ratios 3 and 4. SUPERQUAD calculations prove that the major species, Zn(HL)L⁺, reached maximum concentrations, 80−85 % of C₇M, at pH ≈ 7.1 around these two inflection points. In the further increase

Figure 14. An example of the concentration distribution of the cobalt(II) species vs. pH with 1-(2-pyridinyl)ethanone oxime.

The zinc(II) solutions were in the presence of sufficient ligand excess still stable in the pH range 9−10. The ZH curves (Figure 15) show complex formation already in the pH range 2−3. A weak inflection point appeared at C₇H:C₇M = −1 in the titration curves of solutions with C₇L:C₇M ratios 3 and 4. SUPERQUAD calculations prove that the major species, Zn(HL)L⁺, reached maximum concentrations, 80−85 % of C₇M, at pH ≈ 7.1 around these two inflection points. In the further increase
of pH, Zn\textsubscript{2}L\textsubscript{2}(OH)\textsubscript{2} displaces Zn(HL)L\textsuperscript{+} as major species. With cadmium(II), a colorless precipitate appeared in the C\textsubscript{L}:C\textsubscript{M} = 4 titration at pH ca. 9.0 and in the C\textsubscript{L}:C\textsubscript{M} = 3 titration at pH ca. 9.7. With the addition of more NaOH, the precipitates dissolved in the pH range 11.3–11.5. In backward titrations with HCl, the precipitates reappeared when the pH fell below 10.

SUPERQUAD calculations gave the best $\chi^2$ and $s$ statistics for almost identical models of mono- and binuclear complexes for zinc(II) ($\chi^2 = 25.2$, $s = 2.10$; 425 data points from eight titrations) and

Figure 15. Part of the experimental data plotted as $Z_H$ curves vs. pH for zinc(II) and cadmium(II) complex formation with 1-(2-pyridinyl)ethanone oxime HL. The full lines have been calculated using sets of proposed stability constants in Table 4. The lowest line refers to the ligand alone.
cadmium(II) ($\chi^2 = 30.0, s = 2.35; 456$ data points from eight titrations). The proposed complexes and their stability constants are given in Table 4. Examples of the concentration distributions of the zinc(II) and cadmium(II) species are given in Figures 16 and 17, respectively.

Figure 16. Examples of the concentration distribution of the zinc(II) species vs. pH with 1-(2-pyridinyl)ethanone oxime.

The 1-(2-pyridinyl)ethanone oxime complexes of type $M(HL)_2^{2+}$ are clearly more stable but generally about 1–2 log units weaker acids than the corresponding pyridine-2-aldoxime complexes.
The increased electron density on the oxime NOH group by the methyl —CH₃ group strengthens the NO—H bonds and also the N—M²⁺ bonds. The values of the conventional stability constants calculated according to equation (31) show that the 1-(2-pyridinyl)ethanone oxime complexes ZnL₂ (log β₂ = 11.99), CdL⁺ (log β₁ = 5.31), CdL₂ (log β₂ = 10.02), and Cd₂L₂OH⁺ (log β₃ = 4.30) are in actual fact more stable than the corresponding pyridine-2-aldoxime complexes (10.58, 4.75, 9.09, and 4.30).

Figure 17. Examples of the concentration distribution of the cadmium(II) species vs. pH with 1-(2-pyridinyl)ethanone oxime.
In the crystalline roughly square-planar 1-(2-pyridinyl)ethanone oxime complex PtL₂ the oximate groups are \textit{trans} oriented\textsuperscript{96} and undoubtedly also in the aqueous ZnL₂ and CdL₂.

Zn(HL)\textsuperscript{2+} disappear in the pH range 7.5–8.0 (Figure 16). If its pK\textsubscript{a} = 7.5–8.0, the detection of ZnL\textsuperscript{+} is very difficult with SUPERQUAD. ZnL\textsuperscript{+} dimerizes easily via two oximato \textendash NO\textendash bridges to Zn₂L\textsubscript{2}\textsuperscript{2+}, which hydrolyzes with the increase of pH to Zn₂L₂OH\textsuperscript{+} and Zn₂L₂(OH)\textsubscript{2}. Zn₂L₂(OH)\textsubscript{2} displaces the bis complexes Zn(HL)L\textsuperscript{+} and ZnL₂ as main species in the pH range 8–9 (Figure 16) even in the presence of fourfold ligand excess.

The Cd\textendash O bonds seem to be weaker than in the pyridine-2-aldoxime complexes, because the 1-(2-pyridinyl)ethanone oxime ion is a harder Lewis base and favors more hydrogen H\textsuperscript{+} ion over cadmium(II) ion. Thus, the amounts of Cd₂L₂OH\textsuperscript{+} and Cd₂L₂(OH)\textsubscript{2} remain small. CdL\textsuperscript{+} rather binds the free ligand HL with \textit{cis} orientation of the oxime and oximate groups according reaction (33). The formed \textit{cis}-Cd(HL)L\textsuperscript{+} is stabilized by the intramolecular hydrogen bonding (O\textendash H\cdots\cdot\cdot\cdot O), and its stepwise stability constant of Cd(HL)L\textsuperscript{+} log (β\textsubscript{112}/β\textsubscript{111}) = 2.63 > log β\textsubscript{011} = 2.370. The \textit{trans} orientation of their oxime and oximate groups yields \textit{trans}-Cd(HL)L\textsuperscript{+}, which deprotonates in the pH range 7–10 to CdL\textsubscript{2}. In the pH range 9–10, CdL₂ is the main species in the presence of sufficient ligand excess (Figure 17).

The 1-(2-pyridinyl)ethanone oxime and 6-methylpyridine-2-aldoxime complexes Zn₂L₂OH\textsuperscript{+} (pK\textsubscript{a} = 7.98 and 8.29, respectively) are unlike the corresponding pyridine-2-aldoxime complex (pK\textsubscript{a} = 9.36) considerably more acidic than the aqua Zn\textsuperscript{2+} ion (9.15). Also the 1-(2-pyridinyl)ethanone oxime complex Cd₂L₂OH\textsuperscript{+} (pK\textsubscript{a} = 9.83) is more acidic than the aqua Cd\textsuperscript{2+} ion (11.8). This is surprising, because only one \textendash OH\textendash bridge can exit at the same time in Zn₂L₂(OH)\textsubscript{2} and Cd₂L₂(OH)\textsubscript{2}, if the coordination spheres are still octahedral. The methyl \textendash CH\textsubscript{3} groups accelerate the forward deprotonation reaction

\[
\frac{k_D}{k_R} \text{M}_2\text{L}_2\text{OH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{M}_2\text{L}_2(\text{OH})_2 + \text{H}_3\text{O}^+ \tag{34}
\]

through increasing the bending vibrations of the (MNO)\textsubscript{2} rings but retard the backward recombination reaction through expelling hydrogen/oxonium (H\textsuperscript{+}/H\textsubscript{3}O\textsuperscript{+}) ions. The substitution of the hydrogen atoms of ammonia (NH\textsubscript{3}) with methyl \textendash CH\textsubscript{3} groups decreases the rate constant (k\textsubscript{R}) of the recombination of proton (H\textsuperscript{+}) in aqueous solution at 25 °C from \textit{4.3}⋅10\textsuperscript{10} M\textsuperscript{−1} s\textsuperscript{−1} with NH\textsubscript{3}, to \textit{3.7}⋅10\textsuperscript{10}, \textit{3.1}⋅10\textsuperscript{10}, and \textit{2.5}⋅10\textsuperscript{10} M\textsuperscript{−1} s\textsuperscript{−1} with NH\textsubscript{2}CH\textsubscript{3}, NH(CH\textsubscript{3})\textsubscript{2}, and N(CH\textsubscript{3})\textsubscript{3}, respectively.\textsuperscript{97} In other recombination reactions of H\textsuperscript{+} the rate constants (k\textsubscript{R}) are in aqueous solution at 25 °C, for example, with OH\textsuperscript{−} \textit{1.3}⋅10\textsuperscript{11}, with HS\textsuperscript{−} \textit{7.5}⋅10\textsuperscript{10}, with \textit{meta}-nitrophenol \textit{4.2}⋅10\textsuperscript{10}, with \textit{para}-nitrophenol \textit{3.6}⋅10\textsuperscript{10},\textsuperscript{98} with \textit{UO}_2\textsuperscript{2+} \textit{1.65}⋅10\textsuperscript{10}, \textit{99} with \textit{CuOH}^− \textit{1.10}⋅10\textsuperscript{10}, \textit{100} with \textit{Co(NH}_3\textsubscript{3})\textsubscript{2}\textsuperscript{2+} \textit{4.8}⋅10\textsuperscript{9}, \textit{101} and with \textit{AlOH}^2+, \textit{4.4}⋅10\textsuperscript{9} M\textsuperscript{−1} s\textsuperscript{−1}.\textsuperscript{100} They seem to decrease by a factor 0.3–0.5 for each added positive charge unit to the reaction partner.\textsuperscript{100} If the recombination rate constant k\textsubscript{R} of H\textsuperscript{+}/H\textsubscript{3}O\textsuperscript{+} with the uncharged
pyridine-2-aldoxime and 1-(2-pyridinyl)ethanone oxime complexes Zn$_2$L$_2$(OH)$_2$ are about $4 \times 10^{10}$ and $2 \cdot 10^{10}$ M$^{-1}$ s$^{-1}$, respectively, the deprotonation rate constant $k_D$ of their parent complexes Zn$_2$L$_2$OH$^+$ are about 15–20 and 200 s$^{-1}$, respectively.

3.4. Pyridine-2-carboxamidoxime complexes

Pyridine-2-carboxamidoxime or pyridine-2-amidoxime is a derivative of pyridine-2-aldoxime, where the aldoxime hydrogen is replaced by an amide $\text{─NH}_2$ group. Orama and Saarinen$^9$ have determined its protonation and acidity constants and the stability constants of its copper(II) and nickel(II) complexes in aqueous 0.1 M Na(Cl) solution at 25 °C. In this work, the stability constants have been determined for cobalt(II), zinc(II), and cadmium(II) complexes.

The free pyridine-2-carboxamidoxime HL ($pK_a = 11.7$) is a clearly weaker acid$^9$ than 1-(2-pyridinyl)ethanone oxime (10.87) and pyridine-2-aldoxime (10.00) in 0.1 M Na(Cl) solution.$^{11}$ Also acetaldoxime ($pK_a = 12.36$) are in NaCl solution at 0.3 M ionic strength$^{102}$ weaker acids than acetoxime ($pK_a = 12.42$ at 24.9 °C)$^{92}$ acetophenone oxime (11.48)$^{91}$ acetaldoxime (11.82)$^{90}$ and benzaldoxime (10.7) at low ionic strength.$^{50}$ The electron-withdrawing benzene or pyridine ring decreases but the delocalization of the lone electron pair of the amide nitrogen increases the electron density on the oxime NOH group more that the methyl $\text{─CH}_3$ group does. The increased electron density strengthens the NO$\text{─H}$ bond and also the N$\text{─H}^+$ bond in the protonated ligand H$_2$L$^+$. However, the protonation is slightly weaker in pyridine-2-carboxamidoxime HL ($\log \beta_{101} = 3.798 \pm 0.006$) than in 1-(2-pyridinyl)ethanone oxime (3.968 ± 0.003). The free uncharged pyridine-2-carboxamidoxime HL exists in the crystalline state$^{103,104}$ and according IR data also in solution$^{105}$ as the syn isomer, and the amide $\text{─NH}_2$ group and the pyridine nitrogen atom are on the same side of the C(2)$\text{─C}_{\alpha}$ bond (conformation II below). This conformation is caused by the electrostatic repulsion forces between the lone electron pairs of the oxime (H$_2$N═C═N═OH $\leftrightarrow$ H$_3$N$^{\text{+}}$═C$\cdot\cdot\cdot$N$\cdot\cdot\cdot$OH) and pyridine nitrogens and by the intramolecular hydrogen bonding between amide hydrogens and the pyridine nitrogen (N$\cdot\cdot\cdot$H$\cdot\cdot\cdot$N). However, the complex formation of the ligand HL occurs through the pyridine and oxime nitrogens, which requires the rotation of the
amidoxime group about the C(2)—C\text{\textsubscript{ox}} bond (to conformation I).\textsuperscript{104} Apparently, the rotation also occurs, when the ligand HL protonates to H\textsubscript{2}L\textsuperscript{+}, because the conformation I allows a stronger intramolecular hydrogen bonding N—H\textsuperscript{+}···N—OH between the pyridine and oxime nitrogens. 2-aminoacetamidoxime\textsuperscript{1} (log \(\beta_{101} = 7.942\)) and its N-alkyl\textsuperscript{1,2,4} derivatives (7.214–8.260) protonate undoubtedly in their amino groups and, at low pH, their amidoxime groups also protonate with stepwise protonation constants log (\(\beta_{201}/\beta_{101}\)) = 1.351–2.467 in 1.0 M Na(ClO\textsubscript{4}),\textsuperscript{1} in 0.1 M Na(ClO\textsubscript{4}),\textsuperscript{2} or in 1.0 M Na(Cl) solution.\textsuperscript{4} However, no accurate value for the second protonation constant \(\beta_{201}\) has been determined for pyridine-2-carboxamidoxime.\textsuperscript{9} The reasons are the short distances between the amide, oxime, and pyridine nitrogens, and the repulsion forces between the protons and amide hydrogens. In addition, the pyridine ring is much more rigid than the 2-aminoacetamidoxime molecules. According \textsuperscript{1}H NMR spectra acetamidoxime (log \(\beta_{101} = 5.78\) at 0.0 M ionic strength) and according UV/VIS spectra also benzamidoxime (4.85) protonate in their oxime nitrogens (H\textsuperscript{+}—NOH), not in their amide nitrogens.\textsuperscript{102}

The pink color of cobalt(II) ion was changed to yellowish or brownish already while adding the ligand to the solutions. Only one solution (\(C_M = 7.26\) mM, \(C_L = 7.23\) mM) was clearly pink in the beginning of titration. Also, it was changed to brownish already after the first addition of NaOH. When titrating and enhancing of pH, the solutions were darkened. The attainments of equilibria became very slow already at pH 3.67–4.73. In the end of titration, the solutions were yellowish or dark brown. On standing overnight, they became slightly darker and their yellowish tone weakened. No observed precipitate was formed from the solutions. No structure of the complexes could be determined with X-ray diffraction.

SUPERQUAD analysis showed only two deprotonated complexes Co(HL)L\textsuperscript{+} and Co(HL)\textsubscript{2}L\textsuperscript{+} formed in addition to Co(HL)\textsubscript{2}\textsuperscript{+}, Co(HL)\textsubscript{2}\textsuperscript{2+}, and Co(HL)\textsubscript{3}\textsuperscript{2+}. The fit to the experimental data was not good: \(\chi^2 = 32.0\) and \(s = 3.92\) with \(\sigma_f = \pm 0.02\) ml and \(\sigma_e = \pm 0.1\) mV. The \(Z_H\) curves (Figure 18) did not exceed the zero level, showing that the deprotonated complexes were not formed in large amounts. The high \(Z_H\) values of the 1:1 titrations point to the presence of protonated complexes with H\textsubscript{2}L\textsuperscript{+} as ligand. After the tests of many species, SUPERQUAD analysis showed that only protonated complex with \(pqr\) combination 123 and probable formula Co\textsubscript{2}(HL)\textsubscript{2}H\textsubscript{2}L\textsubscript{5+} showed satisfactory fit with experimental data. Because the stable pH ranges were very narrow, their lower limits in calculation of the stability constants were chosen to 1.80, where the weighting coefficients of the titration points were small (in general between \(\pm 3.0\)) in spite of the great liquid junction potential. The stability constants are given in Table 5. SUPERQUAD analysis rejected all the deprotonated polynuclear complexes. Examples of the concentration distribution of the species are in Figure 19.

The Co(HL)\textsubscript{2}L\textsuperscript{+} complex was only observable in the presence of fivefold ligand excess, where its concentration was in maximum 12–13 % of \(C_M\). This is the reason to the very great inaccuracy of
its stability constant log $\beta_{-113} = 5.1 \pm 0.3$. The model of Table 5 without Co(HL)$_2$L$^+$ gave $\chi^2 = 6.00$ and $s = 1.84$.

Figure 18. Part of the experimental data plotted as $Z_H$ curves vs. pH for cobalt(II) complex formation with pyridine-2-carboxamidoxime HL. The full lines have been calculated using sets of proposed stability constants in Table 5. The lowest line refers to the ligand alone.

The slow attainment of equilibria already in the pH range 3.7–4.8 depending on the solution can be due to the slow reactions of the formed cobalt(III) complexes, and also the color changes for the solutions in the night. The brown color of the solutions formed during titrating never disappeared during backward titrating with HCl solution. This indicates that the oxidation reactions are irreversible. Because of the oxidation of the low spin cobalt complexes the stable pH range left very narrow. No polynuclear complexes except Co$_2$(HL)$_2$H$_2$L$_5^{5+}$ could be observed yet in the pH range 4.0–4.8. The little $\chi^2$ and $s$ values, however, indicate that the amounts of the possible cobalt(III) complexes were yet small in the used pH ranges.

The zinc(II) solutions could be titrated to pH range 7.0–8.4, but the cadmium(II) solution with $C_L:C_M = 3–4$ could be titrated to pH range 9–10. In the $C_L:C_M = 5$ titration of cadmium(II) a precipitate appeared at pH = 9.3 also with this ligand. The $Z_H$ curves (Figure 20) show complex formation for both of the metal ion already in the pH range 2–3. The model of mono and bis complexes with oximato and hydroxo bridged binuclear complexes Zn$_2$L$_2^{2+}$, Zn$_2$L$_2$OH$^+$, and Zn$_2$L$_2$(OH)$_2$ observed with the previous ligands proved unsatisfactory ($\chi^2 = 44.6$ and $s = 2.99$). Addition of a tetranuclear species with the $pqr$ combination –644 to the model gave a considerably better fit to the data. Some binuclear species Zn$_2$L$_2^{2+}$ or Zn$_2$L$_2$OH$^+$, but not Zn$_2$L$_2$(OH)$_2$, also seem to be formed in the pH range 7–8. In
this pH range, the hydrolyzed species Zn₂L₂OH⁺ is more probable. The cadmium(II) complexes are less stable and undergo less polymerization. The SUPERQUAD program calculated stability constants for CdL⁺ and the pqr combination –644 but rejected the pqr combination –322.

Table 5. Proposed formulas and stability constants of pyridine-2-carboxamidoxime complexes relating to the reaction

$$\text{pH}^+ + q\text{M}^{2+} + r\text{HL} \rightleftharpoons (\text{H}^+)_p(\text{M}^{2+})_q(\text{HL})_r$$
in aqueous 0.1 M Na(Cl) solution at 25 °C. a

<table>
<thead>
<tr>
<th>p</th>
<th>q</th>
<th>r</th>
<th>Proposed formula</th>
<th>log β_pqr±3σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>M(HL)²⁺</td>
<td>3.94±0.04</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>1</td>
<td>M(HL)²⁺</td>
<td>7.51±0.04</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>3</td>
<td>M(HL)³⁺</td>
<td>10.44±0.06</td>
</tr>
<tr>
<td>−1</td>
<td>1</td>
<td>1</td>
<td>ML⁺</td>
<td>−6.53±0.07</td>
</tr>
<tr>
<td>−1</td>
<td>1</td>
<td>2</td>
<td>M(HL)⁻¹</td>
<td>2.44±0.21</td>
</tr>
<tr>
<td>−2</td>
<td>1</td>
<td>2</td>
<td>ML₂⁺</td>
<td>−6.84±0.12</td>
</tr>
<tr>
<td>−1</td>
<td>1</td>
<td>3</td>
<td>M(HL)²⁻¹</td>
<td>5.1±0.3</td>
</tr>
<tr>
<td>−2</td>
<td>1</td>
<td>3</td>
<td>M(HL)L⁻¹</td>
<td>−3.99±0.09</td>
</tr>
<tr>
<td>−3</td>
<td>1</td>
<td>3</td>
<td>ML₁⁻</td>
<td>−14.84±0.09</td>
</tr>
<tr>
<td>−3</td>
<td>2</td>
<td>2</td>
<td>M₂L₂OH⁺</td>
<td>−14.32±0.22</td>
</tr>
<tr>
<td>−6</td>
<td>4</td>
<td>4</td>
<td>M₄L₄(H)⁻²⁺</td>
<td>−24.96±0.13</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>M₂(HL)₂H₂L₃⁻⁺</td>
<td>16.22±0.08</td>
</tr>
</tbody>
</table>

| Number of points/titrations | 202/6 | 407/7 | 379/8 | 400/8 |
| χ²                          | 6.55  | 30.3  | 15.5  | 48.6  |
| s                           | 1.73  | 1.7   | 2.15  | 1.44  |
| Ref.                        | II    | IV    | IV    |       |

a The protonation and acidity constants of the free ligand (HL) and the stepwise stability and acidity constants of Cu(HL)²⁺ are given in Table 6.

SUPERQUAD calculations gave the best χ² and s statistics for almost identical models of mono- and binuclear complexes for zinc(II) (χ² = 15.5, s = 2.15; 379 data points from eight titrations) and cadmium(II) (χ² = 48.6, s = 1.44; 400 data points from eight titrations). The proposed complexes and their stability constants are given in Table 5. Examples of the concentration distributions of the zinc(II) and cadmium(II) species are given in Figure 21.

The pyridine-2-carboxamidoxime complexes of type M(HL)²⁺ and M(HL)₃²⁺ are generally slightly more stable, but about 2–3 pKₐ₁ units weaker acids than the corresponding 1-(2-pyridinyl)ethanone oxime complexes (Table 6). The delocalized lone electron pair of the amide nitrogen lengthens the N—OH distances and strengthens the NO—H and N—M²⁺ bonds more than the methyl —CH₃ group. The N—OH distances are in the free pyridine-2-carboxamidoxime HL 1.419–
1.420 Å\(^{103,104}\) in other free amidoximes 1.415–1.438 Å\(^{106–110}\) and in amidoxime complexes generally 1.395–1.426 Å\(^{111–119}\) but in free aldoximes, ketoximes and in their complexes only 1.35–1.39 Å\(^{64,93,94}\).

Figure 19. Examples of the concentration distribution of the cobalt(II) species vs. pH with pyridine-2-carboxamidoxime.

Co(HL)\(_2^2^+\) (pK\(_{a1}\) = 5.07) and Co(HL)\(_3^2^+\) (5.3) are about 2–3 log units stronger acid than Ni(HL)\(_2^2^+\) (7.76), Zn(HL)\(_2^2^+\) (7.80) and Ni(HL)\(_3^2^+\) (8.23) proving that Co(HL)L\(^+\) and Co(HL)\(_2^+\) are low spin. They are easily oxidized to cobalt(III) complexes, which causes the very slow attainment of equilibria in the pH range 3.7–4.8. Co(HL)\(^2^+\), Co(HL)\(_2^2^+\), and Co(HL)\(_3^2^+\) are undoubtedly high spin and reach very high concentrations in the presence of fivefold ligand excess (Figure 19) without observable
oxidation. According to the Irving–Williams stability order,\(^\text{60}\) they are less stable than the corresponding nickel(II) complexes. However, the low spin Co(HL)L\(^+\) (log \(\beta_{112} = 2.44\)) with \(t^2g^6e_g\) electron structure is even more stable than Ni(HL)L\(^+\) (1.76). This proves that Ni(HL)L\(^+\) is high spin and octahedral with \(t^2g^6e_g^2\) electron structure. The approximately equal acidity constants of Ni(HL)\(_2\)\(^{2+}\) (p\(K_{a1} = 7.76\) and p\(K_{a2} = 8.63\)) and Zn(HL)\(_2\)\(^{2+}\) (7.80 and 8.63) prove that Ni(HL)\(_2\)\(^{2+}\) and NiL\(_2\) are also octahedral and high spin.

![Figure 20](image-url)

Figure 20. Part of the experimental data plotted as \(Z_H\) curves vs. pH for zinc(II) and cadmium(II) complex formation with pyridine-2-carboxamidoxime HL. The full lines have been calculated using sets of proposed stability constants in Table 5. The lowest line refers to the ligand alone.
In aqueous 1.0 M Na(ClO₄) solution, 2-aminoacetamidoxime (Hao) and 2-(methylamino)-acetamidoxime (Hma) form orange-colored square-planar low spin complexes Ni(Hao)(ao)⁺ and Ni(Hma)(ma)⁺,¹ showing that Ni(Hao)₂⁺ (p𝐾ₐ = 6.57) and Ni(Hma)₂⁺ (7.10) are considerably stronger acids than Zn(Hao)₂⁺ (8.70), Zn(Hma)₂⁺ (8.54),³ and the 2-(dimethylamino)acetamidoxime complex Ni(Hdma)²⁺ (p𝐾ₐ = 8.76).¹ The crystalline [Ni(Hao)₂(H₂O)₂]Cl₂ is octahedral, the oxime groups are trans-oriented in the equatorial plane and the aqua ligands in the axial position. The Ni–Nox distances are 2.049 Å and N–O distances are 1.426 Å.¹¹¹ The formation of Ni(Hao)₃²⁺ requires that in its parent complex Ni(Hao)₂²⁺ the oxime ligands (Hao) are perpendicularly
coordinated. In the crystalline orange-red \([\text{Ni(Hao)(ao)}]\text{Cl} \cdot 1\frac{1}{2}\text{H}_2\text{O}\), the \(\text{Ni(Hao)(ao)}^+\) molecules are square-planar and arranged so that every nickel(II) atom lies nearly perpendicularly above and below the amide \(\text{—NH}_2\) nitrogen atoms of the adjacent molecules. The Ni—NH\(_2\) distances are 3.189 and 3.325 \(\AA\). The oxime and oximate groups are cis oriented and intramolecular hydrogen bonded in O···O distance of 2.489 \(\AA\).111 The Ni—N\(_{\text{ox}}\) distances are 1.846—1.852 \(\AA\) and the Ni—O(OH) distances are 1.391—1.397 \(\AA\).111 The crystalline \([\text{Ni(Hdma)}(\text{H}_2\text{O})_2]\text{Cl}_2\) is octahedral with bond angles N\(_{\text{ox}}\)─Ni—N\(_{\text{ox}}\) 94.5°, Me\(_2\)N─Ni—NMe\(_2\) 170.2°, and H\(_2\)O—Ni—OH\(_2\) 82.8°, and with Ni—N\(_{\text{ox}}\) distances of 2.064 and 2.086 \(\AA\).111 Apparently, Ni(Hdma)(dma)+ is also octahedral and high spin, because the dimethylamino (Me\(_2\)N—) groups cause steric interference with the planar cis orientation of the oxime and oximate groups.

Table 6. Stepwise stability and acidity constants of pyridine-2-carboxamidoxime complexes of type M(HL)\(_{\text{rz}}\)\(^+\) in aqueous 0.1 M \(\text{Na(Cl)}\) solution at 25 °C.

\[
\begin{array}{ccccccccccc}
\text{M}^+ & \log K_1 & pK_{1a} & \log K_2 & pK_{2a1} & pK_{2a2} & \log K_3 & pK_{3a1} & pK_{3a2} & pK_{3a3} & \text{Ref.} \\
\hline
\text{H}^+ & 3.798±0.006^b & 11.7^c & & & & & & & & 9 \\
\text{Co}^{2+} & 3.94 ±0.04 & 3.57 & 5.07 & 2.93 & 5.3 & & & & & II \\
\text{Ni}^{2+} & 4.93 ±0.10 & 4.59±0.06 & 7.76 & 8.60 & 4.40±0.03 & 8.23 & 9.68 & 10.85 & & 9 \\
\text{Cu}^{2+} & ≥6^d & 4.72±0.03 & 4.61±0.03 & & & & & & & 9 \\
\text{Zn}^{2+} & 3.03 ±0.02 & 2.44 & 7.80 & 8.63 & & & & & IV \\
\text{Cd}^{2+} & 2.53 ±0.01 & 9.06 & 1.64 & 8.45 & 9.16 & & & & & IV \\
\end{array}
\]

\(\text{a}\) The stability constants \((K_i)\) relate to the reaction \(\text{M(HL)}_{\text{rz}}^+ + \text{HL} \rightleftharpoons \text{M(HL)}_{\text{rz}}^{2+}\). The acidity constants are for clarity symbolized as \(K_{1a}, K_{2a1}, K_{2a2}\), and \(K_{3a}\). All the constants have been calculated disregarding the isomers using for example concentrations \([\text{M(HL)}_{\text{rz}}^{2+}] = \Sigma[\text{cis-M(HL)}_{\text{rz}}^{2+}] + \Sigma[\text{trans-M(HL)}_{\text{rz}}^{2+}], b = \log \beta_{101} (\text{M(HL)}^+ = \text{H}_2\text{L}^-). \quad c = -\log \beta_{101}. \quad d\) It could not be experimentally determined, because the formation Cu(III)\(^2+\) was complete already at pH = 2. Its lower limit was estimated by using following data of a solution: \(C_M = C_L = 4.997 \text{ mM}\) and \(Z_{\text{H}}\approx 0 (\approx\text{constant})\) in pH range 2–3 (Figure 1 in Ref. 9).

\(\text{Zn(Hao)}^{2+} (pK_a = 8.70)\) and \(\text{Zn(Hma)}^{2+} (8.54)\) are weaker acids than \(\text{Zn(HL)}^{2+} (7.80)\), and also the free 2-aminoacetamidoxime \((p\beta_{101} = 12.5 ± 0.1)\), 2-(methylamino)acetamidoxime \((12.4 ± 0.1)\), and 2-(dimethylamino)acetamidoxime \((12.3 ± 0.1)\) are weaker acids than the free pyridine-2-carboxamidoxime \((11.7)\).9 The electron-withdrawing pyridine ring increases the acidity of the oxime NOH group but lowers basicity of the pyridine and oxime nitrogens. Thus, copper(II), nickel(II), and zinc(II) ions form less stable complexes with pyridine-2-carboxamidoxime \((\log \beta_{101} = 3.798)\) than with 2-aminoacetamidoxime \((7.942)\) and 2-(methylamino)acetamidoxime \((8.260)\).1 In aqueous 1.0 M \(\text{Na(ClO)}_4\) solution, the free 2-(dimethylamino)acetamidoxime \((\log \beta_{101} = 7.606)\) is a stronger base and Cu(Hma)\(^2+\) \((\log \beta_{011} = 6.909 ± 0.005)\) and Cu(Hdma)\(^2+\) \((\log \beta_{012} = 11.894 ± 0.009, \log K_2 = 4.985)\)
more stable than in 0.1 M Na(ClO)₄ solution (log β₁₀₁ = 7.214, log β₀₁₁ = 6.602 ± 0.006, log β₀₁₂ = 11.284 ± 0.021), and log K₂ = 4.682. Due to the steric interference by the dimethylamino (Me₂N─) groups, Ni(Hdma)²⁺ (log β₀₁₁ = 3.979), Ni(Hdma₃)²⁺ (log β₀₁₂ = 5.52, log K₂ = 1.54), Zn(Hdma)²⁺ (log β₀₁₁ = 2.500), and Zn(Hdma)₂²⁺ (log β₀₁₂ = 4.19, log K₂ = 1.69) are less stable than the corresponding pyridine-2-carboxamidoxime complexes. Zn(Hdma)(dma)¹ and Zn(dma)₂ cannot be observed, because the uncomplexed aqua Zn²⁺ ion precipitates as Zn(OH)₂ in the pH range 7.0–7.5.

Also, Ni(ao)₂, Ni(ma)₂, Ni(dma)₂, Zn(ao)₂, and Zn(ma)₂ don’t reach measurable concentrations in the pH range 8–9, where the precipitation or very slow attainment of equilibria in their solutions begins. Ni(Hao)(ao)⁺ displaces Ni(Hao)₃²⁺ as the main species in the pH range 8.0–8.5 and reaches about 80 % of Cₘ in the presence of fourfold ligand excess in the pH range 8.5–9.0. Ni(Hao)₃²⁺ does not deprotonate, although its proportion at pH = 9 is still about 20 % of Cₘ. Due to the steric requirements by the N-methyl groups the proportion of Ni(Hma)₃²⁺ remains only about 20 % of Cₘ even in the presence of 15-fold ligand excess, and Ni(Hma)(ma)⁺ reaches in the presence of fourfold ligand excess about 95 % of Cₘ. This means that the pKₐ value of cis-Ni(Hma)(ma)⁺ is at least 10–11. Apparently, the amide —NH₂ hydrogens form with their adjacent oxime and oximate oxygens some intramolecular hydrogen bonding N—H⋯O—H⋯O⋯H—N strengthened also by the delocalization of the lone electron pair of the amide —NH₂ nitrogens.

ZnL₂ is probably formed in the pH range 7–8 (Figure 20) through deprotonation of trans-Zn(HL)₂²⁺ via trans-Zn(HL)L⁺, Ni(Hao)₂²⁺, Ni(Hma)₂²⁺, and Ni(Hdma)₂ disappear in the pH range 8–9 and the proportion of Ni(Hdma)(dma)⁺ remains only at about 5 % of Cₘ in the presence of fourfold ligand excess. Apparently also the proportions of the possible trans-Ni(Hao)(ao)⁺ and trans-Ni(Hma)(ma)⁺ remain so small that Ni(ao)₂ and Ni(ma)₂ cannot reach measurable concentration.

The octahedral high spin pyridine-2-carboxamidoxime complexes Ni(HL)₂L⁺ and NiL₂ cannot displace Ni(HL)₃²⁺ (pKₐ = 8.23), Ni(HL)₂L⁺ (9.68), Ni(HL)L₂ (10.85), and NiL₃⁻. In the crystalline [Ni(HL)₃](NO₃)₂·H₂O the oxime groups are mer oriented with Nₐx—N—Nₐx angles of 88.1, 96.8, and 171.1°. Apparently, the structure retains in the protonation of Ni(HL)₃²⁺ stepwise to NiL₃⁻. The formation of mer-Ni(HL)₂²⁺ requires the parent complex trans-Ni(HL)₃²⁺ with perpendicularly coordinated ligands HL (pyridine rings). However, other isomers of Ni(HL)₃²⁺ are also possible.

The crystalline [Ni(HL)₂(NO₃)₂] is distorted octahedral with cis-oriented nitrate NO₃⁻ ions coordinated as monodentate ligands and trans-oriented oxime NOH groups. The Ni—Nₐx bonds (2.048 Å) are shorter, and the Nₐx—Ni—Nₐx angle (168.7°) is slightly smaller than those in the corresponding 1-(2-pyridinyl)ethanone oxime complex (2.059 and 2.069 Å, and 169.88°, respectively). The structures of [M(HL)₂(OOCCH₃)₂], where M = Ni, Zn, or Cd, are similar with bond lengths: Ni—Nₐx 2.054, Zn—Nₐx 2.110, and Cd—Nₐx 2.315 Å, and following angles
N_{ox}–Ni–N_{ox} 166.2,\textsuperscript{113} N_{ox}–Zn–N_{ox} 161.0,\textsuperscript{114} and N_{ox}–Cd–N_{ox} 159.0°,\textsuperscript{115} Also, the structure of [Zn(HL)\textsubscript{2}(OOCPh)\textsubscript{2}] is similar with bond lengths Zn–N_{ox} 2.133 Å, Zn–N_{py} 2.2.03 Å, and the N_{ox}–Zn–N_{ox} angle of 156.7°.\textsuperscript{114} The pyridine nitrogens are generally 0.06–0.10 Å further form the central atom than the oxime nitrogens. The oxime groups are able to form intramolecular hydrogen bonds with the uncoordinated oxygen atoms of the adjacent monodentate acetate −OOCCH\textsubscript{3} or phenolate −OOCPh ligand and also with the adjacent amide −NH\textsubscript{2} hydrogens (N–H⋯O–H⋯OC). In [Ni(HL)\textsubscript{2}(OOCCH\textsubscript{3})\textsubscript{2}] the NOH⋯OC distances are 1.73 Å (NO⋯OC distances are 2.561 Å) and the N–H⋯OH distances are 2.23 Å (N⋯O distances are 2.589 Å).\textsuperscript{113} In the other complexes the NOH⋯OC distances are 1.77–1.86 Å (O⋯O distances are 2.544–2.600 Å).\textsuperscript{114,115} In aqueous acidic solution the monodentate ligands are readily replaced by aqua ligands, but the structure of the bis complexes with perpendicularly trans oriented oxime groups is preserved. The repulsive forces between the partially positively charged aqua and oxime hydrogens can leads to dissociation of the aqua ligand allowing isomerization of the trans-M(HL)\textsubscript{2}\textsuperscript{2+} to cis-M(HL)\textsubscript{2}\textsuperscript{2+}, which is deprotonated at a sufficiently high pH to cis-M(HL)L\textsuperscript{+} stabilized by the intramolecular hydrogen bonding between the oxime and oximate oxygens and their adjacent amide hydrogens N–H⋯O–H⋯O⋯H–N.

It must be noted that the stepwise logarithmic stability differences between Co(HL)\textsuperscript{2+} and Co(HL)\textsubscript{2}\textsuperscript{2+} log (K\textsubscript{1}/K\textsubscript{2}) = 0.37 and between Ni(HL)\textsuperscript{2+} and Ni(HL)\textsubscript{2}\textsuperscript{2+} (0.35) are smaller than the statistic difference between octahedral mono and bis complexes (0.68).\textsuperscript{79} Also log (K\textsubscript{2}/K\textsubscript{3}) between Ni(HL)\textsubscript{2}\textsuperscript{2+} and Ni(HL)\textsubscript{3}\textsuperscript{2+} is small (0.19) but markedly greater between Co(HL)\textsubscript{2}\textsuperscript{2+} and Co(HL)\textsubscript{3}\textsuperscript{2+} (0.64). The statistically small stability differences show significant strengthening of the ligand fields from Ni(HL)\textsubscript{3}\textsuperscript{2+} to Ni(HL)\textsubscript{3}\textsuperscript{2+} and from Co(HL)\textsubscript{2}\textsuperscript{2+} to Co(HL)\textsubscript{2}\textsuperscript{2+}. The aqueous Co(HL)\textsubscript{2}\textsuperscript{2+} may be partly tetrahedral and able to form also fac-Co(HL)\textsubscript{3}\textsuperscript{2+}. Due to the repulsion forces between the positively charged oxime protons fac-Co(HL)\textsubscript{3}\textsuperscript{2+} is less stable than mer-Co(HL)\textsubscript{3}\textsuperscript{2+}. It is also possible that Co(HL)\textsubscript{3}\textsuperscript{2+} is partly low spin (if the energy level difference between its the t\textsubscript{2g} and e\textsubscript{g} orbitals is Δ\textsubscript{o} ≈ 15 000 cm\textsuperscript{-1} or ≈180 kJ/mole).\textsuperscript{51} Apparently, the Co–N distances are about 1.8–1.9 Å in the xy plane of the low spin Co(HL)\textsubscript{2}\textsuperscript{2+} but due to the Jahn–Teller distortion about 2.6–2.7 Å on the z axis of the complex. For example, in the crystalline oxamide dioximato complex [Co(Hoad)\textsubscript{2}−H\textsubscript{2}oad the cobalt(II) ions are low spin chelated by two oxamide dioximato Hoad\textsuperscript{−} anions in s-cis conformation through their oxime NOH and oximate NO\textsuperscript{−} nitrogens in Co–N_{ox} distances of 1.885–1.889 Å.\textsuperscript{116} The adjacent oxime and oximate groups form two intramolecular hydrogen bridges in O⋯O distances of 2.561 Å in the chelate molecules. The individual chelate molecules Co(Hoad)\textsubscript{2} are stacked in the lattice parallel to each other so that the amide −NH\textsubscript{2} nitrogen occupy the fifth and sixth coordination of the cobalt(II) from the upper and lower chelate molecules. The Co–NH\textsubscript{2} distances of 2.639 Å are smaller than the sum of van der Waals radii (3.25 Å) of nitrogen (1.55 Å) and cobalt (1.70 Å).\textsuperscript{116,117}
So the cobalt(II) ions are rather in Jahn–Teller distorted octahedral than in square-planar coordination environments. The brick-red [Ni(Hoad)₂]·H₂oad has very similar structure. The interplanar distances along the stacks are 3.22 and 3.23 Å, but Ni–NH₂ distances are only 3.04 Å proving some bonding interaction between Ni and the axial NH₂ groups.

Apparently, the low spin Co(HL)₂⁺ decomposes completely by Jahn–Teller distortion, but in Co(HL)₂L⁺ the oxime and oximate group and also the amide groups are able to intramolecular hydrogen bonding N–H···O–H···O–H···O–H···N stabilizing the Jahn–Teller distorted complex, especially if the oxime and oximate groups are fac oriented. The intramolecular hydrogen bonding can also cause significant deviation of the axial Co–N bonds form the z axis so that they are short enough to form chelate rings.

In [Zn(HL)₂NO₃]NO₃ the Zn–Nox distances are 2.088 and 2.122 Å, and the Zn–Npy distances are 2.084 and 2.086 Å. The nitrato NO₃⁻ ligand is at the borderline of anisobidentate/monodentate: one of its O–Zn distances is 2.180 Å, but the other is 2.470 Å. The O–Zn–O angle of 53.0(1)° is abnormally small for an octahedral coordination environment. If the oxygen atom in the longer O…Zn distance is considered non-bonding, the geometry about Zn can be described as much distorted trigonal bipyramidal, with the trans oriented oxime nitrogens at the Nox–Zn–Nox angle of 173.3° occupying the axial positions. The angles of the shorter O–Zn with the pyridine nitrogens (O–Zn–Npy) are 98.1 and 145.9°, and the Npy–Zn–Npy angle is 114.9°. In 0.1 M Na(Cl) solution, the water activity is so high that the only nitrato NO₃⁻ ligand of Zn(HL)₂NO₃⁺ is replaced by two rather than one aqua ligand. In the absence of ligand field stabilization, the aqua ligands are readily dissociated, allowing for the isomerization of Zn(HL)₂⁺.

The crystalline [Cu(HL)₂(H₂O)]Cl₂ is square-pyramidal: the ligands HL lie on the bottom with trans oriented oxime NOH groups and the aqua ligand lies on the top of the pyramid. The Cu–Nox distances are 1.969–1.971 Å, the Cu–OH₂ distance is 2.238–2.248 Å, and the Nox–Cu–Nox angle is 172.8°. All attempts to prepare cis-Cu(HL)₂(H₂O)Cl₂ by Pearse et al. were unsuccessful. Apparently, the repulsive forces between the positively charged oxime protons caused in rotation of the oxime OH groups around the N–OH bonds expel the oxime groups from the cis positions.

In aqueous 0.1 M Na(Cl) solution Cu(HL)₂²⁺ is probably octahedral and the oxime ligands (HL) are trans-oriented on the xy plane of the complex and the aqua ligands on its z axis. Due to the Jahn–Teller distortion, the Cu–OH₂ bonds are weak. The dissociation of one aqua ligand allows the isomerization of trans-Cu(HL)₂²⁺ to cis and following deprotonation to Cu(HL)L⁺. The octahedral Co(HL)₂²⁺ can also isomerize via tetrahedral Co(HL)₂²⁺, but Co(HL)L⁺ can also be formed through coordination of free ligand HL to Co(HL)²⁺ with cis orientation of the oxime groups and following
deprotonation already in the pH range 2–3 (Figure 19). Zn(HL)L+ can be formed in a similar way in the pH range 6–8, where the proportion of Zn(HL)2+ is high (Figure 21). Thus, the cis-M(HL)2+ complexes can be much stronger acids but probably much less stable than their trans isomers.

Cd(HL)L+ is formed partly in a similar way than Zn(HL)L+ but mainly through coordination of free HL to CdL+ with cis orientation of the oxime and oximate groups. According to the stepwise stability constants Cd(HL)L+ (log (β−112/β−111) = 2.25) is more stable than Cd(HL)2+ (log (β012/β011) = 1.64) but less stable than Cd(HL)2+ (log β011 = 2.53) and even less stable than the corresponding 1-(2-pyridinyl)ethanone oxime complex Cd(HL)L+ (log (β−112/β−111) = 2.63). The amidoximate oxygen is able to intramolecular hydrogen bonding in CdL+ both with the adjacent aqua ligand and with the amide hydrogens (N–H–O···H2O–Cd). The methyl –CH3 group is hydrophobic but the amide –NH2 is hydrophilic and able also to intermolecular hydrogen bonding hydrogen with the water molecules (N–H···OH2···O–N). Both the intramolecular and the intermolecular hydrogen bonding retard the forward coordination reaction of HL to CdL+ and the hydrogen bonding between them (C=N–O–H···H2O–N–Cd).

CdL2 is formed partly through the deprotonation of trans-Cd(HL)2+ via trans-Cd(HL)L+ but mainly through the coordination of HL to CdL+ with trans orientation of the oxime and oximate groups and following deprotonation. Due to the weak acidity of the oxime NOH group of the free HL (pβ−101 = 11.7) the formation of CdL+ and CdL2 via reaction (32) is very small in the pH range 7–10. For the same reason, the stability constants and even also the conventional stability constants of CdL+ (log β1 = 5.17) and CdL2 (log β2 = 9.96, log K2 = 4.72) are smaller than those of the corresponding 1-(2-pyridinyl)ethanone oxime complexes (log β1 = 5.31, log β2 = 10.02, and log K2 = 4.71).

The weakly acidic pyridine-2-carboxamidoxime does not form binuclear complex Zn2L22+ with the six-membered (ZnNO)2 ring until in the pH range 7.0–7.5, where it is immediately deprotonated. The deprotonation of an aqua ligand leads to the formation of Zn2L2OH+ with a hydroxo –OH− bridge besides the (ZnNO)2 ring, but also the amide groups of Zn2L22+ are deprotonable to form a tetramer. The structure of the tetramer is probably Zn4(L–H)2L22+ with a (ZnNO)2 central ring and two amidoximate (ZnNO)2 bridges (Figure 22). Ji et al.120,121 found that the reaction of NiX2·nH2O (X− = Cl−, Br−, NO3−, ClO4−) with pyridine-2-carboxamidoxime in aqueous acetonitrile solution (pH 9–10) produce red brown single-, double-, or triple-decker complexes, where two nickel(II) ions in square-planar NiN3O environments and two nickel(II) ions in octahedral environments. Aqua ligands have been found only in double- or triple-decker compounds. In the double-decker compounds [Ni4(L–H)2L2(H2O)2]X4·nH2O(CH3CN) (X− = ClO4− and n = 1 or X− = Br− and n = 14 without CH3CN) each of the four octahedral coordination spheres is completed in its axial coordination
position by an aqua ligand and an oximate nitrogen or an oximate oxygen. Thus, the four octahedrally coordinated nickel(II) ions link the adjacent decks by four “pillars” (two Ni–N$_{\text{ox}}$ and two Ni–O$_{\text{ox}}$ bonds). In the triple-decker complexes, the adjacent decks are similarly linked by two Ni–N$_{\text{ox}}$ and two Ni–O$_{\text{ox}}$ bonds and the four octahedrally coordinated nickel(II) ions of two peripheral decks bind four terminal ligands.$^{120}$ Apparently, the formation of double and triple-decker compound instead of single-decker compounds with four aqua ligands is due to the formation of stronger ligand fields. The isolated single-decker compounds [Ni$_4$(L–H)$_2$L$_2$X$_4$](ClO$_4$)$_2$ have been isolated with X = imidazole,$^{120}$ 1-methylimidazole, pyridine, 3- or 4-methylpyridine$^{121}$ coordinated axially to the octahedral nickel(II) ions through nitrogen atoms.

In the single-, double-, or triple-decker complexes the Ni–N/O distances are clearly shorter in the square-planar NiN$_3$O environments (generally 1.812–1.912 Å) than in the octahedral environments (2.009–2.269 Å). The N–O bonds of the doubly deprotonated (L–H)$^{2-}$ ligands bridging two octahedral and one square-planar nickel(II) ions are longer (1.395–1.460 Å) than the N–O bonds of the singly deprotonated L$^-$ ligands bridging one square-planar and one octahedral nickel(II) ions (1.326–1.380 Å).$^{120,121}$ This elongation is likely due to the coordination of the amido –NH$^-$ – groups of the doubly deprotonated ligands.$^{121}$ The Ni$_{\text{oct}}$–N–O–Ni$_{\text{oct}}$ torsion angles of the central (NiNO)$_2$ rings are in the single-decker compounds generally 2.80–13.41° and in the double- and triple-decker compounds generally 11.06–18.70°.$^{120,121}$ The inter-deck Ni–N$_{\text{ox}}$ bond distances are 2.269–2.560 Å, the Ni$_{\text{oct}}$–N–Ni$_{\text{oct}}$ angles are 91.55–93.7°, and the Ni$_{\text{oct}}$–O–Ni$_{\text{oct}}$ angles are 97.37–104.7°.$^{121}$

Figure 22. A proposed schematic representation for the tetranuclear complex ion [Zn$_4$(L–H)$_2$L)$_2$]$^{2+}$ projected in a plane. For clarity, the possible aqua ligands have been omitted.
Pyrazine-2-carboxamidoxime (Hpza) forms in aqueous 0.1 M Na(Cl) solution $\text{Ni}_4(pza–\text{H})_2(pza)^{2+}$ with log $\beta_{644} = –21.70$. It appears in the pH range 7.0–7.5 and its proportion in solution of $C_M = 1$ mM and $C_L = 3$ mM remains almost constant at about 10 % of $C_M$ in the pH range 8–10. Brown $[\text{Ni}_4(pza–\text{H})_2(pza)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2\cdot2\text{H}_2\text{O}$ crystallized from aqueous methanol solution (pH = 9–10) has two square-planar and two octahedral nickel(II) ions, but each octahedrally coordinated nickel(II) ion binds another tetramer in its pyrazine-4-nitrogen atom on the opposite side of the central (NiNO)$_2$ ring. The aqua ligands complete the octahedral coordination. Each tetramer is surrounded by four other tetramers using two pyrazine-4-nitrogens as donor to coordinate with two nickel(II) ions and, in turn, two nickel(II) ions as acceptors for the coordination of two pyrazine-4-nitrogen atoms from another two adjacent tetramers. The Ni–N/O distances are 1.841–1.884 Å in the square-planar NiN$_3$O environments and 2.018–2.136 Å in the octahedral environments. The N–O bonds of the doubly deprotonated (pza–H)$_2^–$ ligands are 1.383 Å. In red-brown single-decker crystals of $[\text{Ni}_4(pza–\text{H})_2(pza)_2\text{Py}_4]X_2\cdot n\text{Py}$ ($X^– = \text{ClO}_4^–$ and $n = 2$ or $X = \text{NO}_3^–$ and $n = 4$) formed by slow diffusion of methanol to pyridine (Py) solution of NiX$_2\cdot6\text{H}_2\text{O}$ the octahedral nickel(II) ions are axially coordinated by two pyridine nitrogen atoms. Apparently, the complete formula of the aqueous tetramer is $\text{Ni}_4(pza–\text{H})_2(pza)_2(\text{H}_2\text{O})_8^{2+}$, where both of the octahedral nickel(II) ions are axially coordinated by two water oxygen atoms.

Pyridine-2-carboxamidoxime does not form polynuclear nickel(II) complexes in aqueous solution. They are apparently displaced by Ni(HL)$_2$ (log $\beta_{213} = –3.99$) and NiL$_3^–$ (log $\beta_{313} = –14.84$), which are much more stable than Ni(Hpza)(pza)$^–$ (log $\beta_{101} = –6.02$) and Ni(pza)$^3–$ (log $\beta_{313} = –16.12$). Also Ni(HL)$_2^{2+}$ (log $\beta_{012} = 9.52$), and Ni(HL)$_3^{2+}$ (log $\beta_{013} = 13.92$) are much more stable than Ni(Hpza)$^2+$(3.36) Ni(Hpza)$^3–$ (5.97), and Ni(Hpza)$^3–$ (8.37). Due to the second electron-withdrawing nitrogen atom, the pyrazine ring is a much weaker base than the pyridine ring. Thus, the free pyrazine (log $\beta_{011} = 0.65$ at 1.0 M ionic strength) is a much weaker base than the free pyridine (log $\beta_{101} = 5.25$ at 0 ionic strength and 5.33 ± 0.01 in NaClO$_4$ solution at 0.1 M ionic strength). From this point of view, the protonation of the free pyrazine-2-carboxamidoxime (log $\beta_{101} = 2.68$) is connected rather to the oxime nitrogen (H$^+$–NOH) as in acetamidoxime (log $\beta_{101} = 5.78$ at 0.0 M ionic strength) and benzamidoxime (log $\beta_{101} = 4.85$) than to the pyrazine-1-nitrogen.

2-(N-dimethylamino)- and 2-(N-diethylamino)acetamidoxime (Hdea) form similar tetranuclear complexes with copper(II) and nickel(II) ions in aqueous solution. The X-ray analysis proved that in the crystalline complexes $[\text{Cu}_4(\text{dma–H})_2(\text{dma}_2)](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ and $[\text{Cu}_4(\text{dea–H})_2(\text{dea}_2)](\text{ClO}_4)_2$ all the four copper(II) atoms are in square-planar environments. In both of the tetramers, the Cu–N/O distances are 1.873–2.054 Å in the square-planar CuN$_3$O environments and 1.89–2.090 Å in the square-planar CuN$_2$O$_2$ environments. The N–O bonds of the doubly deprotonated ligands (dma–H)$^{2–}$ (1.42 Å) and (dea–H)$^{2–}$ (1.431 Å) bridging two copper(II) atoms of the central (CuNO)$_2$ rings and one
copper(II) atom of a CuN₃O environment are also in these tetramers longer than the N─O bonds of the singly deprotonated ligands dma⁻ (1.34 Å) and dea⁻ (1.347 Å) bridging two copper(II) atoms of one CuN₃O and one CuN₂O₂ environments.⁴

The larger size of cadmium(II) ion especially weakens the Cd─O bonds and the polymerization of CdL⁺ in this way. For this reason, the (CdNO)₂ ring is much weaker than the (ZnNO)₂ ring. Cd₄(L─H)₂L₂⁺ is probably formed similar to Zn₄(L─H)₂L₂⁺, but in the higher pH range 8.5–9.0 where the amido bridges outnumber the hydroxo bridges. Although Cd₄(L─H)₂L₂⁺ is the major species in the pH range 9–10, CdL⁺ and CdL₂ are remarkable competing species (Figure 21). In the further increase of pH, Cd₄(L─H)₂L₂⁺ is seemingly displaced by CdL₂. In Zn₄(L─H)₂L₂⁺ and Cd₄(L─H)₂L₂⁺ probably all the zinc(II) and cadmium(II) ions are in in octahedral environments. The square-planar coordination is very improbable for the d¹⁰ structured metal ions.

The connection often found between the composition of the ternary hydrolytic complexes and the binary hydroxo species Cu₂(OH)₂⁺, Ni₄(OH)₄²⁺, and Cd₄(OH)₄²⁺ of the metal ions would suggest competing amidoximato complexes with structures Cu₄(OH)₂L₂⁺, Ni₄(OH)₄(HL)₂L₂⁺, and Cd₂(OH)₄(HL)₂L₂⁺ in aqueous solution. But for zinc(II) complexes, such structures are improbable. The binary hydrolysis of zinc(II) produces only ZnOH²⁺ and Zn₂OH³⁺ before precipitation commences in the neutral region.⁵⁻⁸ Both zinc(II) and cadmium(II) ions form mainly binary complexes ZnImₙ²⁺ and CdImₙ²⁺ (n = 1–4) with imidazole (Im) and only at low C₇:CM ratios in small amounts also ternary complexes Zn(OH)Im⁺, Zn(OH)Im₃⁺, Zn₂(OH)Im₂³⁺, Zn₂(OH)Im₃³⁺, and Cd(OH)Im⁺.¹²⁹ The d¹⁰ electron structures of zinc(II) and cadmium(II) ions favor coordination of nitrogen over oxygen. Thus, the dimer Zn₂L₂⁺ is mainly polymerized via two amido —NH— bridges to Zn₄(L─H)₂L₂⁺, which becomes the major species in the pH range 7.5–8.0 (Figure 21). The proportions of the competing species Zn₂L₂OH⁺ and ZnL₂ in the same pH range remain smaller. This is reflected as relatively large inaccuracies in the values of log β₃²₂ and log β₁₂₁.

The alternative binuclear structure Zn₂(L─H)L⁺ or Zn(L─H)ZnL⁺ with an uncoordinated oximate oxygen (NO⁻) atom in L⁻ can be excluded in the pH range 7.0–7.5. The ternary hydroxo complex Zn₂L₂OH⁺ is much more probable, although in its parent complex Zn₂L₂⁺ (pKₐ < 7.0) the (ZnNO)₂ ring is probably in chair conformation as in Zn₂L₂(acac)₂ crystallized from methanol with the Zn─N─O─Zn torsion angle of 59.5° (and the zinc(II) ions in distorted trigonal bipyramidal ZnN₂O₃ environments).¹¹⁴ In aqueous Zn₂L₂⁺ the (ZnNO)₂ ring is flexible and bends easily to boat conformation, which allows the formation of a hydroxo bridge beside the oximato bridges. In the tetramers Zn₄(L─H)₂L₂⁺ and Cd₄(L─H)₂L₂⁺ the central (MNO)₂ rings are apparently so rigid and that no hydroxo bridge can be formed beside their oximato bridges.

The structure of the binuclear complex Co₂(HL)₂H₂L⁵⁺ is very difficult to predict. It probably involves a combination of Co(HL)²⁺, Co(HL)₂²⁺, and a proton H⁺ that connects the complex nuclei.
with a hydrogen bridge. The bridge is broken by the deprotonation of \( \text{H}_2\text{L}^+ \) to HL. \( \text{Co}_2(\text{HL})_2\text{H}_2\text{L}^{5+} \) reaches its maximum concentration in the pH range 1.7–2.1 and disappears in the same pH range (3.2–3.7), where \( \text{Co(HL)L}^+ \) appears (Figure 19).

3.5. Pyridine-2-acetamidoxime complexes

Orama and Saarinen\(^9\) have determined for pyridine-2-acetamidoxime the protonation and acidity constants and the stability constants for its copper(II) and nickel(II) complexes in aqueous 0.1 M Na(Cl) solution at 25 °C. In this work, the stability constants have been determined for cobalt(II), zinc(II), and cadmium(II) complexes.

In the free pyridine-2-acetamidoxime HL (\( \log \beta_{101} = 5.017 \pm 0.003 \))\(^9\), the protonation is about 0.2–0.3 log units weaker than in the free pyridine (\( \log \beta_{101} = 5.25 \) at 0 ionic strength,\(^{48} 5.33 \pm 0.01 \) at 0.1 M ionic strength in NaClO\(_4\) solution\(^{49}\)) and about 0.7–0.8 log units weaker than in the free acetamidoxime (\( \log \beta_{101} = 5.78 \) at 0.0 M ionic strength).\(^{102}\) The \(-\text{CH}_2-\) group effectively isolates the amidoxime group and the pyridine nitrogen and allows also the amide \(-\text{NH}_2\) group to protonate with a stepwise protonation constant \( \log (\beta_{201}/\beta_{101}) = 2.29 \pm 0.01 \).\(^9\) This protonation is of same order or higher than in 2-aminoacetamidoxime (\( \log (\beta_{201}/\beta_{101}) = 2.467 \)) and in its \( N \)-alkyl derivatives (1.351–2.112),\(^1,2,4\) but 1–2 log units smaller than in 3-amnopropanamidoxime (4.005) and in its \( N \)-alkyl derivatives (3.660–3.823).\(^5,7\) At low pH the free rotations around the \( \text{C}--\text{C} \) bonds allow intramolecular hydrogen bonding between the pyridine (or amino) and oxime nitrogens (\( \text{N}--\text{H}^+\cdot\cdot\cdot\text{N} \)) and in the higher pH range between the amide hydrogens and pyridine (or amino) nitrogens (\( \text{N}--\text{H}\cdot\cdot\cdot\text{N} \)). The oxime dissociation is in the free pyridine-2-acetamidoxime HL (\( p\text{K}_a = 12.3 \)) weaker or about equally weak than in the free pyridine-2-carboxamidoxime (11.7),\(^9\) 2-aminoacetamidoxime (12.5),\(^1\) 3-aminopropanamidoxime (11.5),\(^5\) and in their \( N \)-alkyl derivatives (12.0–12.4),\(^1,5,7\) but clearly stronger than in the free acetamidoxime (\( p\text{K}_a = 13.21 \) in NaCl solution at 0.3 M ionic strength).\(^{102}\) The increased acidity of 3-aminopropanamidoxime (\( p\text{K}_a = 11.5 \)) is probably due to the intramolecular hydrogen bonding between the amino, oximate, and amide groups (\( \text{N}--\text{H}\cdot\cdot\cdot\text{N}--\text{O}\cdot\cdot\cdot\text{H}--\text{N} \)).

The formation of the cobalt(II) complexes could be followed up to pH range 6.0–6.2. Also, these cobalt(II) ion solutions changed during titrating from pink to yellow and finally to brown. Formation and oxidation of some low spin cobalt(II) complexes was observed in the SUPERQUAD calculation. All of the solutions with a more than twofold excess of ligand led to large \( \chi^2 \) and \( s \) values and had to be removed from the SUPERQUAD calculation, which was run with only three solutions. The \( Z_H \) curves of the solutions are shown in Figure 23. The stability constants are given in Table 7 with the
earlier determined stability constants of the copper and nickel(II) complexes and the protonation constants of the ligand (HL) used in the SUPERQUAD calculation.

Table 7. Stability constants (log $\beta_{pqr}$) of pyridine-2-acetamidoxime complexes relating to reaction $pH^+ + qM^{2+} + rHL \rightleftharpoons (H^+)p(M^{2+})q(HL)_r$ in aqueous 0.1 M Na(Cl) solution at 25 °C.

<table>
<thead>
<tr>
<th>$M^{2+}$</th>
<th>log $\beta_{111}$</th>
<th>log $\beta_{011}$</th>
<th>log $\beta_{012}$</th>
<th>log $\beta_{--111}$</th>
<th>log $\beta_{--112}$</th>
<th>log $\beta_{--222}$</th>
<th>log $\beta_{--322}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>7.307±0.013$^a$</td>
<td>5.017±0.003$^b$</td>
<td>−12.3$^c$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>6.0 ±0.5</td>
<td>2.56 ±0.05</td>
<td>4.73±0.07</td>
<td>−1.87±0.14</td>
<td></td>
<td></td>
<td></td>
<td>II</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>3.59 ±0.01</td>
<td>6.86±0.02</td>
<td>−1.56±0.05</td>
<td>−13.82±0.02</td>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>5.31 ±0.01</td>
<td>9.55±0.03</td>
<td></td>
<td>4.7±0.1</td>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>1.79 ±0.02</td>
<td></td>
<td>−16.29±0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>1.72 ±0.02</td>
<td>−8.05±0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV</td>
</tr>
</tbody>
</table>

$a = \log \beta_{201}$. $^b = \log \beta_{101}$. $^c = \log \beta_{-101}$.

The proposed formulas of the cobalt(II) complexes in Table 7 are from left to right: Co(H$_2$L)$_3^{3+}$, Co(HL)$_2^{2+}$, Co(HL)$_2^2^+$ and Co(HL)L$^+$. This model gives $\chi^2 = 7.87$ and $s = 1.28$ with $\sigma_E = \pm 0.1$ mV and $\sigma_V = \pm 0.02$ ml. The SUPERQUAD program rejects all other stability constants. The addition of a solution with $C_M: C_L \approx 1:3$ to the used series of the three solutions gives greater stability constants to all complexes in Table 3 with $\chi^2 = 82.6$ and $s = 3.86$. This indicates the formation of low spin cobalt(II) complexes in the increase of pH and their increasing oxidation to cobalt(III) complexes in the presence of a great ligand excess. The SUPERQUAD program interprets the formed cobalt(III) complexes probably as Co(HL)$_2^{2+}$ and Co(HL)L$^+$ and a part of complexes Co(HL)$_2^{2+}$ as Co(HL)$_2^{+}$. This leads to un reliably great stability constants for the three complexes.

Co(HL)L$^+$ (log $\beta_{--112} = −1.87$) is only 0.3 log units less stable than Ni(HL)L$^+$ (−1.56), although Co(HL)$_2^{2+}$ (log $\beta_{012} = 4.73$) is over two log units less stable than Ni(HL)$_2^{2+}$ (6.86). This proves that Co(HL)L$^+$ is low spin, but Co(HL)$_2^{2+}$, Co(HL)$_2^{2+}$, and Co(HL)$_2^{3+}$ are high spin. Co(H$_2$L)$_3^{3+}$ (log $\beta_{111} = 6.0 \pm 0.5$) exists at low pH and deprotonates to Co(HL)$_2^{2+}$ with $pK_a \approx 3.4$. Analogous complexes are also formed by 3-aminopropanamidoxime and its $N$-methylated derivatives with cobalt(II)$^8$ and copper(II) ions.$^5$ The positively charged pyridinium or ammonium group must be sufficiently far from the central metal ion (there are five atoms between the positive charges), and the chelate ring is possibly not closed. No polynuclear cobalt(II) complexes could be found. An example on the concentration distribution of the cobalt(II) species in solutions is given in Figure 24.

The zinc(II) solutions could be titrated only to pH range 7.0–7.5 and cadmium(II) solutions to pH range 8–9. The slight dispersion of the $Z_{II}$ curves (Figure 25) demonstrates only weak complex formation for both metal ions. The $Z_{II}$ curves exceed the zero level in the end of the titrations proving
some formation of deprotonated complexes. SUPERQUAD calculations gave the best $\chi^2$ and $s$ statistics for models $\text{Zn(HL)}^{2+}$ and $\text{Zn}_2\text{L}_2\text{OH}^+$ ($\chi^2 = 11.7, s = 1.47, 255$ points from eight titrations) and $\text{Cd(HL)}^{2+}$ and $\text{CdL}^+$ ($\chi^2 = 39.7, s = 1.11, 230$ points from eight titrations). The stability constants are given in Table 7. Examples of the concentration distributions of the zinc(II) and cadmium(II) species are given in Figure 26.

![Figure 23](image)

**Figure 23.** Part of the experimental data plotted as $Z_H$ curves vs. pH for cobalt(II) complex formation with pyridine-2-acetamidoxime HL. The full lines have been calculated using sets of proposed stability constants in Table 7. The lowest line refers to the ligand alone.

![Figure 24](image)

**Figure 24.** An example of the concentration distribution of the cobalt(II) species vs. pH with pyridine-2-acetamidoxime.

$\text{Zn}_2\text{L}_2\text{OH}^+$ is probably formed through dimerization of two deprotonated $\text{Zn(HL)}^{2+}$ complexes ($\text{ZnL}^+$) via two oximato $\text{─NO}^\text{─}$ bridges to $\text{Zn}_2\text{L}_2^{2+}$, which in the pH range $7.0–7.5$ immediately
deprotonates to \( \text{Zn}_2\text{L}_2\text{OH}^+ \) through forming a hydroxo \(-\text{OH}^-\) bridge besides the six-membered \((\text{ZnNO})_2\text{L}_2\) ring. Nickel(II) ion forms an analogous complex \( \text{Ni}_2\text{L}_2\text{OH}^+ \).\(^9\) Cadmium(II) \( \text{Cd}^{2+} \) does not deprotonate until in the pH range 8–9. Although the proportion of \( \text{CdL}^+ \) was small in all the solution (Figure 26), it was accepted because it would be very difficult to find reasons to exclude the deprotonation of the parent complex \( \text{Cd}^-\text{HL}^2+ \) in the pH range 8.0–8.8. \( \text{Cd}(\text{HL})_2^+ \) (\( pK_a = 9.77 \)) is, as expected, about 0.7 \( pK_a \) units weaker acid than the corresponding pyridine-2-carboxamidoxime complex (9.06). Similar to this is the calculated acidity difference between the \( \text{Ni}(\text{HL})_2^{2+} \) complexes with pyridine-2-acetamidoxime (\( pK_a = 8.42 \)) and with pyridine-2-carboxamidoxime (7.76).\(^9\) The small amounts of

---

**Figure 25.** Part of the experimental data plotted as \( Z_H \) curves vs. pH for zinc(II) and cadmium(II) complex formation with pyridine-2-acetamidoxime HL. The full lines have been calculated using sets of proposed stability constants in Table 7. The lowest line refers to the ligand alone.
CdL⁺ explains the slight exceeding of the $Z_H$ curves above the zero level before the precipitation of Cd(OH)$_2$.

![Graph showing concentration distributions of zinc(II) and cadmium(II) species vs pH with pyridine-2-acetamidoxime.](image)

Figure 26. Examples of the concentration distributions of the zinc(II) and cadmium(II) species vs pH with pyridine-2-acetamidoxime.

Due to the six-membered chelate rings, the complex formation of the pyridine-2-acetamidoxime with zinc(II) and cadmium(II) ions is very small. The cobalt(II), nickel(II), and copper(II) complexes are stabilized by ligand fields. The stepwise logarithmic stability differences $\log (K_1/K_2)$ between Co(HL)$_2^2+$ ($\log K_1 = 2.56$) and Co(HL)$_2^3+$ ($\log K_2 = 2.17$) and between Ni(HL)$_2^2+$ ($\log K_1 = 3.59$) and Ni(HL)$_2^3+$ ($\log K_2 = 3.27$) are (0.32–0.39) smaller than the statistic difference between octahedral
mono and bis complexes \((0.68)\).\(^{79}\) \(\text{Cu(HL)}_2^{2+}\) \((\log \beta_{011} = 5.31)\) and \(\text{Cu(HL)}_2^{2+}\) \((\log \beta_{012} = 9.55)\) are even more stable\(^9\) than the corresponding pyridine-2-aldoxime complexes \((\log \beta_{011} = 3.93\) and \(\log \beta_{012} = 7.48)\).\(^{11}\) Also, the 3-aminopropanamidoxime complexes \(\text{Ni(ap)}^{2+}\) \((\log \beta_{011} = 4.89)\) and \(\text{Ni(ap)}^{2+}\) \((\log \beta_{012} = 8.35)\) are even more stable\(^8\) than the corresponding pyridine-2-aldoxime complexes \((\log \beta_{011} = 4.19\) and \(\log \beta_{012} = 7.62)\) in 1.0 M Na(Cl) solution,\(^{10}\) but the corresponding pyridine-2-acetamidoxime complexes \(\text{Ni(HL)}^{2+}\) \((\log \beta_{011} = 3.59)\) and \(\text{Ni(HL)}^{2+}\) \((\log \beta_{012} = 6.86)\) are less stable. The electron-withdrawing pyridine rings weaken also the stabilities of these complexes as the basicity of the free ligand HL. Thus, the pyridine nitrogen of the free pyridine-2-acetamidoxime \((\log \beta_{011} = 5.017)\) is a much weaker base than the amine nitrogens of 3-aminopropanamidoxime \((9.061)\) and its \(N\)-alkyl derivatives \((8.577–9.375)\).\(^5\)–\(^7\) All these oximes form with copper(II) and nickel(II) ions pentanuclear complexes, and the crystal structure has been determined by X-ray diffraction for the solid 3-(\(N\)-methylamino)propanamidoxime complex \([\text{Cu}_5(\text{mp–H})_4]\text{Br}_2\cdot2\text{H}_2\text{O})\(^5\) The pentamer consists of four \(\text{Cu(mp–H)}\) units linked together via amido \(\text{NH}^–\) and oximato \(\text{NO}^–\) bridges, from which the oximato bridges are branched to form a square-planar \(\text{CuO}_4\) central core. In the aqueous pentanuclear nickel(II) complexes, the central core is probably octahedral \((\text{NiO}_6)\) with two aqua ligands. This structure allows the deprotonation of \(\text{Ni}_5(\text{ap–H})_4^{2+}\) to \(\text{Ni}_5(\text{ap–H})_4\text{OH}^+\). \(\text{Ni}_5(\text{ap–H})_4^{2+}\) \((\text{pK}_a = 9.6)\), \(\text{Ni}_5(\text{mp–H})_4^{2+}\) \((9.4)\), and the 3-(\(N\)-dimethylamino)propanamidoxime complex \(\text{Ni}_5(\text{dmp–H})_4^{2+}\) \((9.5)\) are weak acids\(^7\) as the aqua \(\text{Ni}^{2+}\) ion \((\text{pK}_a = 9.85)\).\(^{28}\) \(\text{Ni}_5\text{L}_2\text{OH}^+\) is probably formed via two oximato \(\text{NO}^–\) bridges and a hydroxo \(\text{OH}^–\) bridge between the nickel(II) ions. At high \(\text{C}_L:\text{C}_M\) ratios a precipitate or slow attainment of equilibria appears in the pH range 8–9 and at low \(\text{C}_L:\text{C}_M\) ratios in the pH range 7–8. \(\text{Cu}_2\text{L}_2^{2+}\) is formed at lower pH ranges \((\text{pH} < 5.9)\) only via two oximato \(\text{NO}^–\) bridges. The available pH ranges remain too narrow to observe possible tetra- or pentanuclear pyridine-2-acetamidoxime complexes.\(^9\)

3.6. Pyridine-2,6-dicarboxamidoxime complexes

Pyridine-2,6-dicarboxamidoxime is a tridentate ligand with two amidoxime groups. Because both of the oxime groups are deprotonable, it is best to symbolize the uncharged form of the ligand as \(\text{H}_2\text{L}\) instead of HL. In evaluating the equilibrium constants, the binary two-component equilibria \((35–41)\) are considered:

\[
\text{H}^+ + \text{H}_2\text{L} \rightleftharpoons \text{H}_3\text{L}^+; \beta_{101}
\]

\[(\text{35})\]

\[
2\text{H}^+ + \text{H}_2\text{L} \rightleftharpoons \text{H}_4\text{L}^{2+}; \beta_{201}
\]

\[(\text{36})\]
\[ H_2L \rightleftharpoons H^+ + HL^-; \quad K_{a1} \]  \hspace{1cm} (37)

\[ HL^- \rightleftharpoons H^+ + L^{2-}; \quad K_{a2} \]  \hspace{1cm} (38)

\[ M^{2+} + H_2L \rightleftharpoons M(H_2L)^{2+}; \quad K_{011} \]  \hspace{1cm} (39)

\[ M(H_2L)^{2+} + H_2L \rightleftharpoons M(H_2L)_2^{2+}; \quad K_{012} \]  \hspace{1cm} (40)

In evaluation the stability constants of the three-component \((H^+, M^{2+}, \text{and } H_2L)\) equilibria equation (11) is replaced with

\[ pH^+ + qM^{2+} + rH_2L \rightleftharpoons (H^+)_p(M^{2+})_q(H_2L)_r; \quad \beta_{pqr} \]  \hspace{1cm} (41)

Bovenzi and Pearse\(^{130}\) have reported the crystal structures of the solid ligand \(H_2L\), \([Cu(H_2L)SO_4] \cdot 2H_2O\), and \([Ni(H_2L)_2]SO_4 \cdot 5H_2O\). In this work the protonation and acidity constants of the free ligand \(H_2L\) and the stability constants for its copper(II) and nickel(II) complexes in aqueous 0.1 M Na(Cl) solution at 25 °C have been determined. To find out the role of the deprotonation of the oxime function on these complexes, the crystal structure of \([Ni(HL)_2] \cdot 4H_2O\) has also been determined.

To determine the values of protonation and acidity constants only ligand added to the solution of 50.00 ml 0.100 M NaCl + 7.00 ml 0.1 M HCl after the determination of \(E_0\). The solutions were then titrated with the accurately known 0.1 M NaOH solution. Only dilute solutions could be used without precipitation. In solution with an initial \(C_L \geq 3 \text{ mM}\), a white precipitate was formed already at pH 3–4 and dissolved again in the pH range 10–11. Titration points after the dissolution had to be used in data treatment to determine of the acidity constants \(K_{a1}\) and \(K_{a2}\). The protonation and acidity constants calculated from 246 titration points of five titration with \(\chi^2 = 8.37\) and \(s = 1.75\) are shown in Table 8. The values of constants \(\log \beta_{101} = 3.817\) and \(pK_{a1} = 11.2\) prove that the precipitate was formed by the uncharged ligand \(H_2L\).

Bovenzi and Pearse\(^{130}\) used infrared stretching assignments of \(NH_2\) and \(OH\) groups to show that there are considerable intermolecular hydrogen bonds between the adjacent ligand molecules \((H_2L)\) in the solid state involving amide and oxime hydrogens with oxime oxygens \((N-H\cdots O\text{ and } O-H\cdots O)\) and with amide nitrogens \((N-H\cdots N\text{ and } O-H\cdots N)\).\(^{130}\) Every uncharged ligand molecule \((H_2L)\) has four groups capable of intermolecular hydrogen bonding, which probably promotes the precipitation in aqueous solution.

The interactions of the amidoxime groups in pyridine-2,6-dicarboxamidoxime \(H_2L\) can be understood by comparing its acidity constants \((pK_{a1} = 11.2, \ pK_a = 12.2)\) with those of pyridine-2-carboxiamidoxime\(^9\) \((pK_a = 11.7)\) and benzamidoxime\((12.36 \text{ in aqueous NaCl solution at } I = 0.3 \text{ M})\).\(^{102}\) Comparable acidity differences are found between pyridine-2,6-dialdoxime \((pK_{a1} = 9.7\text{ and }pK_{a2} =}
10.7 in NaClO₄ solution at \( I = 0.01 \) M\(^{131}\), pyridine-2-aldoxime (\( pK_a = 10.17 \) at \( I < 0.001 \) M\(^{47}\), and benzaldoxime (10.7 at low ionic strength)\(^{50}\). The pyridine nitrogen increases the acidity of the 2-amidoxime and 2-aldoxime groups by 0.5–0.7 log units and the additional 6-amidoxime or 6-aldoxime group by about 0.5 log units. Pyridine-2,6-dialdoxime (\( \log \beta_{101} = 2.34 \)) is in NaClO₄ solution at 0.005 M ionic strength\(^{131}\) a much weaker base than pyridine-2-aldoxime (\( \log \beta_{101} = 3.56 \)) at low (< 0.001 M) ionic strength\(^{47}\). The additional electron-withdrawing 6-aldoxime groups lowers the basicity of the pyridine nitrogen about 1.2 log units, but there are no essential difference between the protonation constants of pyridine-2,6-dicarboxamidoxime \( H_4L \) (\( \log \beta_{101} = 3.817 \pm 0.015 \)) and pyridine-2-carboxamidoxime \( HL \) (3.798 ± 0.006)\(^9\). The increased electron densities by the delocalization of lone electron pairs of the amide nitrogens allow the amidoxime nitrogens to form a much stronger intramolecular hydrogen bonding with pyridine nitrogen (\( H\cdots O\cdots H \cdots N \cdots H \cdots O \)) than the aldoxime groups. In the decrease of pH, pyridinium-2,6-dicarboxamidoxime \( H_3L^+ \) protonates further to \( H_4L^{2+} \) with a stepwise protonation constant \( \log (\beta_{201}/\beta_{101}) = 2.336 \pm 0.015 \). It is of same order with those of pyridine2-acetamidoxime (\( \log (\beta_{201}/\beta_{101}) = 2.29 \pm 0.01 \))\(^9\); 2-aminoacetamidoxime (2.467)\(^1\), and its \( N \)-alkyl derivatives (1.351–2.112)\(^1,2,4\). It was previously estimated that the amide group would be protonated\(^5,9,13\). However, observations of the structures of the protonated acetamidoxime and benzamidoxime\(^{102}\) suggest that the proton would be attached also in other amidoximes to the oxime nitrogen rather than to the amide nitrogen. The protonation of the amidoxime group lowers the basicity of the pyridine nitrogen in ortho position and probably transfers the proton to the other amidoxime nitrogen. Both of the protonated amidoxime groups of \( H_4L^{2+} \) rotate around the \( C_{py} \cdots C_{ox} \) bonds and the pyridine nitrogen forms intramolecular hydrogen bonding with the amide hydrogens (\( N\cdots H \cdots N \cdots H \cdots N \)). Bovenzi and Pearse\(^{130}\) have shown with X-ray analysis that in the crystalline state both of the amide \( \cdots NH_2 \) groups and the pyridine nitrogen of the free \( H_2L \) are on the same side of the \( C_{py} \cdots C_{ox} \) bonds as the only amide group in the crystalline pyridine-2-carboxamidoxime.\(^{103,104}\) This conformation (II below) is probable also in aqueous \( H_2L \) and \( H_4L^{2+} \) because of the intramolecular hydrogen bonding (\( N\cdots H \cdots N \cdots H \cdots N \)) and the repulsion forces between the protons in \( H_4L^{2+} \) or between the lone electron pairs of the oxime (\( H_2N\cdots C\cdots N\cdots OH \leftrightarrow H_2N^+\cdots C\cdots N\cdots OH \)) and pyridine nitrogens in \( H_2L \).
The formation of the copper(II) complexes occurs in very acidic conditions. At beginning of the measurements, the solutions were blue or blueish-green and the green color strengthened during titration. The \( Z_{\text{H}} \) curves (Figure 27) of the solutions show very strong complex formation already at \( \text{pH} = 2 \). The same is true in the system \( \text{Cu}^{2+} \)-pyridine-2-carboxamidoxime. Here, the stability constant of the mono complex \( \text{Cu(H}_{2}\text{L})^{2+} \) could be determined only by using very dilute solutions with \( C_M = 0.347 \text{–} 0.681 \text{ mM} \) and \( C_L = 0.347 \text{–} 0.689 \text{ mM} \) in 1:1 titrations. The best fit to the data from eight titrations and 208 points \( (\chi^2 = 36.7 \text{ and } s = 1.02) \) was obtained with a simple model consisting of mononuclear species \( \text{Cu(H}_{2}\text{L})^{2+}, \text{Cu(H}_{2}\text{L})_{2}^{2+}, \text{Cu(H}_{2}\text{L})\text{HL}^+, \) and \( \text{Cu(HL)}_{2}^{2+} \) (or \( \text{Cu(H}_{2}\text{L})\text{L} \)). Their stability constants are given in Table 8. The useful experimental data were restricted to \( \text{pH} < 6.8 \), preventing further analysis.

Because of the high stability of \( \text{Cu(H}_{2}\text{L})^{2+} \) 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 \( \text{Cu(H}_{2}\text{L})^{2+} \) reported in Table 8 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 28.

Although pyridine-2,6-dicarboxamidoxime (\( \text{H}_{2}\text{L} \)) is a tridentate ligand, \( \text{Cu(H}_{2}\text{L})^{2+} \) (log \( \beta_{011} = 6.66 \pm 0.13 \)) is less stable than the 2-aminoacetamidoxime complex \( \text{Cu(Hao)}^{2+} \) (8.787), and also \( \text{Cu(Hma)}^{2+} \) (8.108) and \( \text{Cu(dma)}^{2+} \) (6.909 in 1.0 M NaClO\(_4\)) despite of the steric requirements by the \( N \)-methyl groups. Even \( \text{Cu(Hap)}^{2+} \) (7.53 ± 0.01) and \( \text{Cu(Hmp)}^{2+} \) (6.82 ± 0.01) are more stable despite their six-membered chelate rings. The electron-withdrawing pyridine ring weakens significantly the basicity of the free pyridine-2,6-dicarboxamidoxime (log \( \beta_{101} = 3.817 \)) and also stability of \( \text{Cu(H}_{2}\text{L})^{2+} \). The free 2-aminoacetamidoxime (log \( \beta_{101} = 7.942 \)) and the free 3-aminopropanamidoxime (9.061) are much stronger bases and able to form more stable metal complexes than the tridentate pyridine-2,6-dicarboxamidoxime.

The stepwise stability constant of \( \text{Cu(H}_{2}\text{L})_{2}^{2+} \) (log \( K_2 = 3.53 \)) is due to the Jahn–Teller distortion much smaller than log \( K_1 = 6.66 \). Attempts to synthesize any crystalline complex with copper(II) chloride were unsuccessful. Bovenzi and Pearse reported that the ligand does not form the expected monomeric product with copper(II) sulfate but rather a two-dimensional Jahn–Teller distorted polymer \( \{[\text{Cu(H}_{2}\text{L})\text{SO}_4]_2\text{H}_2\text{O}\}_n \). Each of the copper–ligand units are bonded to two sulfate groups by Cu—O bonds resulting in five-coordinate copper(II) ions.

The \( Z_{\text{H}} \) curves (Figure 27) show measurable formation of nickel(II) complexes 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 the 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 nine titrations and 265 points \( (\chi^2 = 28.2, s = 1.07) \) was obtained by assuming the mononuclear species
Ni(H$_2$L)$_2^{2+}$, Ni(H$_2$L)$_2^{3+}$, Ni(H$_2$L)HL$^+$, Ni(HL)$_2$, Ni(HL)L$^-$, and NiL$_2^{2-}$. The stability constants and the acidity constants of Ni(H$_2$L)$_2^{2+}$ are given in Table 8.

The stability constant of Ni(H$_2$L)$_2^{2+}$ ($\log \beta_{011} = 5.67 \pm 0.15$) is fairly inaccurate, and it is therefore not clear whether it is more stable than Ni(Hao)$_2^{2+}$ (5.720 ± 0.005). However, unlike Cu(H$_2$L)$_2^{2+}$, it is clearly more stable than Ni(Hma)$_2^{2+}$ (5.253) and Ni(Hap)$_2^{2+}$ (4.89).

Figure 27. Part of the experimental data plotted as $Z_H$ curves vs. pH for copper(II) and nickel(II) complex formation with pyridine-2,6-dicarboxamidoxime H$_2$L. The full lines have been calculated using sets of proposed stability constants in Table 5. The lowest line refers to the ligand alone.
Unlike the copper(II) complexes, the inaccuracy of the stability constant of Ni(H$_2$L)$_2^{2+}$ is not markedly cumulated to the other $\beta$-constants calculated. The overall stability constants of Ni(H$_2$L)$_2^{2+}$, Ni(H$_2$L)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$_2^{2-}$ ($\log \beta_{412} = -27.25 \pm 0.23$) could not be obtained, because the complex was observed in the 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 28.

Table 8. Proposed formulas and stability constants ($\log \beta_{pqr}$) of pyridine-2,6-dicarboxamidoxime complexes relating to the reaction $\text{pH}^+ + q\text{M}^{2+} + r\text{H}_2\text{L} \rightleftharpoons (\text{H}^+)q(\text{M}^{2+})r(\text{H}_2\text{L})$, and their first acidity constants ($pK_a$) in aqueous 0.1 M Na(Cl) solution at 25 °C.

<table>
<thead>
<tr>
<th>$p$</th>
<th>$q$</th>
<th>$r$</th>
<th>Proposed formula</th>
<th>$\log \beta_{pqr} \pm 3 \sigma$</th>
<th>$pK_a \pm 3 \sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>H$_3$L$^+$</td>
<td>3.817 ± 0.015</td>
<td>3.817 ± 0.015</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>H$_4$L$^{2+}$</td>
<td>6.153 ± 0.013</td>
<td>2.336 ± 0.013</td>
</tr>
<tr>
<td>−1</td>
<td>0</td>
<td>1</td>
<td>HL$^-$</td>
<td>−11.2 ± 0.2$^a$</td>
<td>12.2 ± 0.2$^a$</td>
</tr>
<tr>
<td>−2</td>
<td>0</td>
<td>1</td>
<td>L$^2$</td>
<td>−23.4 ± 0.2$^a$</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>Cu(H$_2$L)$_2^{2+}$</td>
<td>6.66 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>Cu(H$_2$L)$_2^{2+}$</td>
<td>3.53$^b$ ± 0.04</td>
<td>4.92 ± 0.05</td>
</tr>
<tr>
<td>−1</td>
<td>1</td>
<td>2</td>
<td>Cu(H$_2$L)HL$^+$</td>
<td>5.23 ± 0.15</td>
<td>6.71 ± 0.12</td>
</tr>
<tr>
<td>−2</td>
<td>1</td>
<td>2</td>
<td>Cu(HL)$_2$ (or Cu(H$_2$L)L)</td>
<td>−1.48 ± 0.20</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>Ni(H$_2$L)$_2^{2+}$</td>
<td>5.67 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>Ni(H$_2$L)$_2^{2+}$</td>
<td>11.31 ± 0.08</td>
<td>8.17 ± 0.04</td>
</tr>
<tr>
<td>−1</td>
<td>1</td>
<td>2</td>
<td>Ni(H$_2$L)HL$^+$</td>
<td>3.14 ± 0.09</td>
<td>9.18 ± 0.04</td>
</tr>
<tr>
<td>−2</td>
<td>1</td>
<td>2</td>
<td>Ni(HL)$_2$</td>
<td>−6.04 ± 0.09</td>
<td>9.96 ± 0.05</td>
</tr>
<tr>
<td>−3</td>
<td>1</td>
<td>2</td>
<td>Ni(HL)L$^-$</td>
<td>−16.00 ± 0.10</td>
<td>11.25 ± 0.22</td>
</tr>
<tr>
<td>−4</td>
<td>1</td>
<td>2</td>
<td>NiL$_2^{2-}$</td>
<td>−27.25 ± 0.25</td>
<td></td>
</tr>
</tbody>
</table>

$^a \pm 10 \sigma$, $^b = \log K_2$ relating to the reaction Cu(H$_2$L)$_2^{2+}$ + H$_2$L $\rightleftharpoons$ Cu(H$_2$L)$_2^{2+}$.

The structure of the crystallized complex with the formula [Ni(HL)$_2$]-4H$_2$O could be determined by X-ray diffraction. A crystal was selected for the X-ray measurement and mounted to the glass fiber using the oil drop method; data were collected at 173 K on Nonius Kappa CCD 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, SHELXS–97, and SHELXS–97–2 were used for data reduction, structure solution, and structure refinement, respectively. The non-hydrogen 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. The crystal structure is orthorhombic, space group *phen* with \( a = 12.601(3) \), \( b = 9.3990(19) \), \( c = 17.195(3) \) Å, \( \alpha = \beta = \gamma = 90° \) and \( Z = 4 \). The structure is shown in Figure 29.

![Figure 28](image)

**Figure 28.** Examples of the concentration distributions of copper(II) and nickel(II) species vs. pH with pyridine-2,6-carboxamidoxime.

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-coordinated through the oxime, oximato and pyridine 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 **Ni→N\(_{py}\) bonds (2.0042 Å)** are shorter...
than in the crystalline octahedral high spin pyridine-2-carboxamidoxime complexes Ni(HL)2(NO3)2 (2.084–2.090 Å),112 Ni(HL)2(OOCCH3)2 (2.116 Å),113 and Ni(HL)32+ (2.079–2.109 Å),112 but only slightly shorter than in [Ni(H2L)2]SO4·5H2O (2.007 Å).130 The Ni—NO− (2.1361 Å) bonds are longer than the Ni—NOH bonds (2.1326 Å) and the N(9)—Ni—N(9A) angle (100.56°) is larger than the N(1)—Ni—N(1A) (96.44°), N(1)—Ni—N(9A), and N(1A)—Ni—N(9) angles (87.70°) apparently because of the repulsion forces between the oximate NO− groups. Due to the rigid structures of the tridentate ligands, the Ni—NOH bonds are also in Ni(H2L)22+ (2.117–2.136 Å) longer than in the octahedral high spin nickel(II) complexes of bidentate amidoximes (2.048–2.086 Å).111–113 In Ni(HL)2 the N—O(H) bond lengths (1.4239 Å) are typical for the octahedral high spin amidoxime complexes112–115 but the N—O− bonds are shorter (1.3752 Å). The deprotonation of the oxime group shortens the N—O bond and opens the C=N—O bond angle, 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) angles are 110.93° but the C=N—O− angles are 115.26°. The C(2)—N(1)—Ni and C(8)—N(9)—Ni angles are 117.15° and 114.45°, respectively, but in Ni(H2L)2 the corresponding angles are 116.3°.130 The C=N—O(H) angles in the free pyridine-2,6-carboxdiamidoxime H2L are

Figure 29. Crystal structure of [Ni(HL)2]·4H2O showing the atomic numbering scheme. The water molecules have been omitted for clarity.
108.7°,130 in the free pyridine-2-carboxamidoxime HL 108.89°,103 or 109.1°,104 and in other free amidoximes generally 109.0–110.7°.106–109 In high spin pyridine-2-carboxamidoxime complexes the C=N–O(H) angles are generally 111.3–112.6°,112–115 and in other amidoxime complexes 110.6–111.8°.111,136,137 The deprotonation of the oxime group opens the C=N–O angles and the intramolecular hydrogen bonding C=N–O–H⋯O–N=C opens also the C=N–OH angles. For example, in the following 1-(2-pyridinyl)ethanone oxime complexes Ni(HL)₂Br₂ the C=N–O(H) angles are 114.7° and 115.3°, in [Ni(HL)L(H₂O)₂]NO₃ the C=N–OH angle is 116.5° and the C=N–O⁻ angle is 119.1°,94 in Cu(HL)LCl the C=N–OH angle is 118.3° and the C=N–O⁻ is 117.7°,93 and in [PtL₂] C=N–O angles are 119.5°.96 In the pyridine-2-aldoxime complex [PtL₂]·2H₂O the C=N–O angles are 119.1°,74 and in the dimeric complex Ni(HL)L₂·6½H₂O the C=N–OH angles are 120.7°, the hydrogen bridged C=N–O⁻ angles are 117.2°, and the non-bridged C=N–O⁻ angles are 118.8°.10 In the octahedral 2-aminoacetamidoxime complex [Ni(Hao)₂(H₂O)₂]Cl₂ the C=N–O angles are 111.6° but in the square-planar [Ni(Hao)(ao)]Cl 1½H₂O 114.8° and 116.3°.111 In mononuclear metal chelates (M = Cu²⁺, Ni²⁺, Zn²⁺, Co³⁺), where all the oxime groups are deprotonated, the C=N–O angles are in general within 119–123°.138,139

The titration and crystallographic analyses (Figure 29) show that the bis complex Ni(H₂L)₂²⁺ dissolves with increasing pH stepwise to Ni(HL)₂, which further dissolves to NiL₂²⁻. According to its conventional stability constant log β₂ = (log β₂-121 + 2pβ-101) = 16.4, Ni(HL)₂ is more stable but according to its acidity constants pKₐ₁ = 9.96 and pKₐ₂ = 11.25 (pKₐ3 and pKₐ4 of Ni(H₂L)₂²⁺, respectively) 2–3 log units weaker acid than the corresponding pyridine-2,6-dialdoxime complex (log β₂ = 15.7, pKₐ₁ = 7.3, pKₐ₂ = 8.9 in NaClO₄ solution at I = 0.01 M).131 The delocalization of the lone electron pairs of the amide NH₂ nitrogens increases electron density in the oxime nitrogens strengthening the Ni–Nₚy and oxime NO–H bonds and weakens the acidity of Ni(HL)₂. The pyridine-2-carboxamidoxime complexes Ni(HL)₂L⁺ (pKₐ = 9.68) and Ni(HL)₂L₂ (pKₐ = 10.85) are clearly weaker acids⁹ than Ni(H₂L)(HL)⁺ (9.18) and Ni(HL)₂ (9.68) and also the pyridine-2-aldoxime complex Ni(HL)L₂ (pKₐ = 7.71 in 1.0 M Na(Cl) solution) is a weaker acid than the pyridine-2,6-dialdoxime complex Ni(HL)₂ (7.3 in NaClO₄ solution at I = 0.01 M).131 The bidentate ligands apparently stabilize Ni(HL)₂L⁺ and Ni(HL)₂L₂ with some intramolecular hydrogen bonding (O–H⋯O⁻–H⋯O and O⋯H ⋅⋅⋅O, respectively). The tridentate ligands are so rigid that no intramolecular hydrogen bonding can be observed in the solid Ni(HL)₂ between the perpendicularly coordinated oxime and oximate groups.

The Jahn–Teller distortion weakens the acidity of the ligand coordinated on the z axis of Cu(H₂L)₂²⁺, explaining the rather large difference between the values of pKₐ₁ = 4.92 and pKₐ₂ = 6.71. Figure 29 shows that in NiH₂L₂ both ligands are present in the form HL⁻ giving the structure Ni(HL)₂.
In the case of the copper(II) complex \( \text{Cu(H}_2\text{L)HL}^+ \), deprotonation to \( \text{Cu(HL)}_2^+ \) is questionable; it is also possible that both of the protons dissociate from the same ligand in the \( xy \) plane giving a complex \( \text{Cu(H}_2\text{L)L} \). Pinart et al.\textsuperscript{140} proposed that the structure of the corresponding pyridine-2,6-dialdoxime complex is \( \text{Cu(HL)}_2 \) with intramolecular hydrogen bonding (\( =\text{N}−\text{O}−\text{H}⋅⋅⋅\text{O}−\text{N}= \)) between the adjacent oxime and oximato groups. In the copper(II) complexes \( \text{Cu(H}_2\text{L)HL}^+ \) and \( \text{Cu(HL)}_2 \), Jahn–Teller distortion can cause such a marked deviation on the \( z \) axis to the ligand that some intramolecular hydrogen bonding is possible. The absence of \( \text{Cu(HL)}^+ \) even in the pH range 6.0–6.7 can be due to forming of deprotonated bis complexes \( \text{Cu(H}_2\text{L)HL}^+ \) and \( \text{Cu(HL)}_2 \) with some stabilizing intramolecular hydrogen bonding. The detection of \( \text{Ni(HL)}^+ \) is difficult, because the proportion of its parent complex \( \text{Ni(H}_2\text{L)}^2^+ \) is small (<5 %) in the pH range 8–9 (Figure 28). Due to the stronger ligand field the stepwise stability constant of \( \text{Ni(H}_2\text{L)}^2^+ \) (\( \log K_2 = 5.64 \)) is nearly equal to that of \( \text{Ni(H}_2\text{L)}^2^+ \) (\( \log K_1 = 5.67 \pm 0.15 \)). In a weaker ligand field, \( \text{Ni(H}_2\text{L)}^2^+ \) is a weaker acid than \( \text{Ni(H}_2\text{L)}^2^+ \) (\( pK_a = 8.17 \)).

4. SUMMARY AND CONCLUSIONS

Pyridine-2-aldoxime and its methyl or amide derivatives coordinate as uncharged ligands HL to metal ions through their pyridine and oxime nitrogens. As Figure 30 shows the stability of the mono complexes \( \text{M(HL)}^2^+ \) increases with few exceptions in the order \( \text{Cd} < \text{Zn} < \text{Co} < \text{Ni} < \text{Cu} \).

Pyridine-2-carboxamidoxime (\( \log \beta_{101} = 3.798 \)) and 1-(2-pyridinyl)ethanone oxime (3.968) are stronger bases and form clearly more stable mono complexes than pyridine-2-aldoxime (\( \log \beta_{101} = 3.590 \)) does. The methyl —CH\(_3\) and amide —NH\(_2\) groups increase the electron density of the oxime and the pyridine nitrogens. The increased electron density strengthens the basicity of the pyridine ring and the oxime NO—H nitrogen weakening the acidity of the oxime NOH group. The three ligands form also bis complexes and with nickel(II) and partly with cobalt(II) ion also tris complexes. Pyridine-2-acetamidoxime and 6-methylpyridine-2-aldoxime don’t form tris complexes because of the six-membered chelate rings and the steric interferences by the 6-methyl groups. Pyrazine-2-carboxamidoxime is taken in Figure 30, because its electron-withdrawing 4-nitrogen significantly weakens the basicity (\( \log \beta_{101} = 2.68 \)) and complexing ability of the ligand. Therefore, the pyrazine-2-carboxamidoxime complexes are less stable than the corresponding pyridine-2-aldoxime complexes. An exception is \( \text{Cu(Hpz)}^2^+ \) (\( \log K_1 = 4.16 \)), which is more stable than \( \text{Cu(Hpyal)}^2^+ \) (3.93). \( \text{Cu(Hpyac)}^2^+ \) (\( \log K_1 = 5.31 \)) is despite its six-membered chelate ring almost as stable as \( \text{Cu(Hpyet)}^2^+ \) (5.63). Pyrazine-2-carboxamidoxime forms tris complexes only with nickel(II) ion. The stepwise stability orders of the complexes \( \text{M(HL)}^r_2^+ \) are with all the ligands: \( K_1 > K_2 > K_3 \).
Figure 30. The stepwise stability constants of the mono complexes $M(HL)^{2+}$ vs. divalent metal ion ($M^{2+}$) and hydrogen ion ($H^+$). Abbreviations: Hpyal = pyridine-2-aldoxime, Hmepy = 6-methylpyridine-2-aldoxime, Hpyet = 1-(2-pyridinyl)ethanone oxime, Hpyca = pyridine-2-carboxamidoxime, Hpyac = pyridine-2-acetamidoxime, Hpza = pyrazine-2-carboxamidoxime. For the metal ions $\log K_1 = \log \beta_{011}$ and for $H^+$ $\log K_1 = \log \beta_{101}$. The stability constant of Ni(Hpyal)$^{2+}$ was determined in 1.0 M Na(Cl), the other constants in 0.1 M Na(Cl) solution, all at 25 °C.

It seems that copper(II) ion favors amidoximes over aldoximes. Ni(Hpyal)$^{2+}$ ($\log \beta_{011} = 4.19$) is in 1.0 M Na(Cl) solution more stable than Cu(Hpyal)$^{2+}$ (3.93) in 0.1 M Na(Cl). This is probably because the free pyridine-2-aldoxime (Hpyal) is in 1.0 M Na(Cl) a stronger base (3.865) than even pyridine-2-carboxamidoxime (Hpyca) in 0.1 M Na(Cl) solution (3.798). However, Ni(Hpyal)$^{2+}$ is in 1.0 M Na(Cl) solution clearly less stable than Ni(Hpyca)$^{2+}$ ($\log \beta_{011} = 4.93$) and Ni(Hpyet)$^{2+}$ (4.98) in 0.1 M Na(Cl) solution. This is probably due the weaker ligand field in the pyridine-2-aldoxime complexes.

In the increase of pH the complexes deprotonate. The deprotonated bis complexes M(HL)L$^+$ are stabilized by an intramolecular hydrogen bridge between the cis oriented oxime and oximate groups ML$_2$, the oxime and oximate groups are probably trans oriented due to the repulsion forces between the negatively charged oximate groups and between the positively charged oxime protons. The complexes are apparently octahedral, and the dissociation of their aqua ligands allows the isomerization of the trans oriented oxime groups to cis. It is also possible that the trans-M(HL)$_2L^+$ complexes deprotonate via trans-M(HL)L$^+$ to trans-ML$_2$. The intermediates trans-M(HL)L$^+$ are much less stable but stronger acids than their cis isomers. In the tris complexes, the oxime groups are apparently mer oriented, and the structure is prevented in the deprotonated nickel(II) complexes Ni(HL)$_2$L$^+$, Ni(HL)L$_2$, and NiL$_3$.$^{-}$.
The cobalt(II) complexes Co(HL)²⁺ and Co(HL)₂²⁺ are mainly octahedral high spin complexes with \( t_2^g e_g^2 \) electron structure, but some tetrahedral complexes also exist with two fully occupied lower \( e \) and three half-occupied higher energy \( t_2 \) orbitals (\( e^4t_2^3 \)) in equilibrium. The bis complexes Co(HL)₂²⁺ are except the pyridine-2-aldoxime complex about 2–3 log units stronger bases than the corresponding Ni(HL)₂²⁺ and Zn(HL)₂²⁺ complexes, because the Co(HL)L⁺ complexes are low spin with \( t_2^g e_g^2 \) electron structure. Pyridine-2-carboxamidoxime forms also tris complex Co(HL)₃²⁺, which deprotonates with \( pK_a = 5.3 \) to Co(HL)₂L⁺. Co(HL)₃²⁺ is probably mainly high spin with \textit{mer} oriented oxime groups, but Co(HL)₂L⁺ is low spin. In Co(HL)₂L⁺ the \textit{mer} oriented oxime and oximate groups are not obvious. The octahedral low spin cobalt(II) complexes are Jahn–Teller distorted because of the uneven electron occupation in their \( e_g \) orbitals. The \textit{fac} oriented oxime and oximate are more capable of intramolecular hydrogen bonding \( \text{O}−\text{H}⋯\text{O}−\text{H}−\text{O} \) in the Jahn–Teller distorted complexes than the \textit{mer} oriented ones. Also, pyridine-2-aldoxime forms Co(HL)₂L⁺, which is low spin, but its parent complex Co(HL)₃²⁺ never reaches measurable concentrations. The low spin cobalt(II) complexes oxidize easily to cobalt(III) complexes, because their only \( e_g \) electron detaches very easily. The \( t_2^g e_g \) electron structured cobalt(III) complexes are very inert and their substitution reactions are very slow. The oxidation of the low spin cobalt(II) complexes is very strong in acid solution but no longer in the pH range 8–10. With the increase in the concentration of low spin cobalt(II) complexes, the attainment of equilibria becomes slow often already in the pH range 4–5. Using very small cobalt(II) ion concentration (\( C_M \leq 0.36 \text{ mM} \)) a pyridine-2-aldoxime solution could be titrated to pH range 8–9, but very small NaOH addings had to be used in the pH range 5–8. In the increase of pH Co(HL)₂L⁺ is completely displaced by CoL₂ and the deprotonated complexes Co(HL)L₂ and CoL₃⁻ never reach measurable concentrations.

It is possible that 1-(2-pyridinyl)ethanone oxime also forms tris complexes with cobalt(II) ion. They cannot be detected, because Co(HL)₂²⁺ (\( pK_{a1} \approx 2.8 \)) is about 2–3 log units stronger acid than Ni(HL)₂²⁺ (4.82) and Zn(HL)₂²⁺ (5.16), Co(HL)L⁺ is low spin and oxidizes to cobalt(III) complex already in the pH range 2.5–2.9. The high spin structure of the pyridine-2-aldoxime complex Co(HL)L⁺ and the weaker acidity of the pyridine-2-carboxamidoxime complex Co(HL)₂²⁺ (\( pK_a = 5.07 \)) allow the detections of the tris complexes with these ligand.

6-methylpyridine-2-aldoxime forms Co(HL)²⁺, CoL⁺, CoL₂, Co₂L₂OH⁺, Co₂L₃⁺, and Co₂L₃OH with cobalt(II) ion. The 6-methyl groups cause steric interference with the \textit{cis} orientation of the oxime groups in a plane. Apparently, CoL₂ is octahedral low spin and due to the Jahn–Teller distortion, at least one of the oximate \( −\text{NO}^- \) groups lies on the \( z \) axis of the complex. Co₂L₃⁺ is probably formed through combination of CoL₂ and CoL⁺ via three oximato \( −\text{NO}^- \) bridges. One of the cobalt(II) ions in CoN₄O₂ environment is probably low spin, but the other in CoN₂O₄ environment is high spin. The octahedral low spin part and one of the oximato bridges is Jahn–Teller distorted. The deprotonation
of Co$_2$L$_3^+$ to Co$_2$L$_3$OH in the pH range 6–9 requires formation of a hydroxo $-$OH $-$ bridge and breaking of an oximato bridge, if the coordination spheres of Co$_2$L$_3$OH are still octahedral. The Jahn–Teller distorted oximato bridge of Co$_2$L$_3^+$ is easily broken and after bending of the remaining (CoNO)$_2$ ring, the hydroxo bridge is formed on the opposite side of the of the opened oximato $-$NO$^-$ group. Co$_2$L$_3$OH$^+$ is probably formed through dimerization of two deprotonate mono complexes (CoL$^+$) via two oximato bridges and a hydroxo bridge between the cobalt(II) ions. Both of the cobalt(II) ions are in CoN$_2$O$_4$ probably high spin.

Pyrazine-2-carboxamidoxime forms similar cobalt(II) complexes, but instead of CoL$^+$ and CoL$_2$, it forms Co(HL)L$^+$ and Co$_2$L$_2$(OH)$_2$. As in Co$_2$L$_3$OH, only three bridges are possible in Co$_2$L$_2$(OH)$_2$ between the cobalt(II) ions, if their coordination spheres are still octahedral. The bending of the (MNO)$_2$ rings easily breaks the hydroxo bridge and causes a collision of two adjacent aqua ligands on the opposite site of the broken hydroxo bridge. One of the two aqua ligands is then released as oxonium H$_3$O$^+$ ion and the other deprotonated to OH$^-$ ligand, which forms a new hydroxo bridge. Soon, the formed hydroxo bridge is broken and the former hydroxo ligand is again bridged. The two hydroxo ligands of M$_2$L$_2$(OH)$_2$ form alternatively short-lived hydroxo bridges between metal ions.

The pyrazine-2-carboxamidoxime complexes Co(HL)L$^+$ and Ni(HL)L$^+$ disappear in the pH range 9–10 without deprotonation to CoL$_2$ and NiL$_2$. In amidoxime complexes, the delocalization of the lone electron pairs of the amide nitrogens stabilize the intramolecular hydrogen bonding between the oxime and oximate oxygen and the adjacent amide hydrogens are also able to intramolecular hydrogen bonding: N$\cdots$H$\cdots$O$\cdots$H$\cdots$N.

Both 6-methylpyridine-2-aldoxime and pyrazine-2-carboxamidoxime form also Ni(HL)$_2^{2+}$ and Ni$_2$L$_3^+$ but neither form Ni$_2$L$_3$OH. The three oximato bridges of Ni$_2$L$_3^+$ must be fac oriented and none of them is Jahn–Teller distorted. If one of the oximate ligands is located in the $xy$ plane of the NiL$_2$ unit (NiN$_4$O$_2$ environment) and the other pyridine nitrogen on the $z$ axis of the unit, none of the three oximato bridges can be replaced by a hydroxo bridge without significant isomerization of the complex. 6-methylpyridine-2-aldoxime forms also NiL$_2$, where the oximate groups are trans oriented and the Ni$\cdots$N$_{py}$ bonds are perpendicular to each other. This structure allows NiL$_2$ to form insoluble polymers with deprotonated mono complexes via oximato and hydroxo bridges starting with Ni$_3$L$_4$(OH)$_2$. In all solutions with $C_L \geq 1.5 \ C_M$, a precipitate or very slow attainment of equilibrium appears already in the pH range 6.5–7.5. 6-methyl groups cause steric interference with the cis orientation of the oxime or oximate groups and with the formation of tris complexes. Pyrazine-2-carboxamidoxime forms soluble tris complexes and a tetramer Ni$_4$L$_2$(L$-$H)$_2^{2+}$ with a (NiNO)$_2$ central ring and two amido $-$NH$^-$ $-$ bridges binding the central Ni$_2$(L$-$H)$_2$ unit and two Ni$^+$ units.

6-methylpyridine-2-aldoxime forms with zinc(II) and cadmium(II) ions only deprotonated complexes: Zn$_2$L$_2^{2+}$ ($p_K_a = 6.31$), Zn$_2$L$_2$OH$^+$ ($8.29$), and Zn$_2$L$_2$(OH)$_2$, CdL$^+$, CdL$_2$, and Cd$_2$L$_2$OH$^+$. In
Zn$_2$L$_2^{2+}$, only two oximato bridges combine the zinc(II) ions. Its proportion remains small, because the hydroxo bridge is already formed in the pH range 6–7 beside the (ZnNO)$_2^+$ ring. The polymerization of CdL$^+$ is rather weak, and the proportion of Cd$_2$L$_2$OH$^+$ remains small.

Also, pyridine-2-aldoxime and 1-(2-pyridinyl)ethane oxide form Zn$_2$L$_2^{2+}$ ($pK_a = 6.54–6.83$) Zn$_2$L$_2$OH$^+$ (7.99–9.36), Zn$_2$L$_2$(OH)$_2$, and Cd$_2$L$_2$OH$^+$ in addition to mono and bis complexes. Pyridine-2-aldoxime forms also Cd$_2$L$_2^{2+}$ ($pK_a = 8.64$) and the 1-(2-pyridinyl)ethane oxide complex Cd$_2$L$_2$OH$^+$ deprotonates with $pK_a = 9.83$ to Cd$_2$L$_2$(OH)$_2$. Due to the larger size of cadmium(II) ion, the cadmium(II) complexes are weaker acids and also the polymerization of CdL$^+$ is rather weak. The pyridine-2-aldoxime complex Zn(HL)$_2^{2+}$ doesn’t reach measurable concentrations. The proportion of Zn(HL)$_2^{2+}$ ($pK_a = 6.71$) is in the pH range 6–7 still so large that ZnL$^+$ reaches measurable concentrations. Similarly, the cadmium(II) complexes CdL$^+$ reach measurable concentrations with all the six oximes. Except the pyridine-2-carboxamidoxime complex, none of the complex of type Cd(HL)$_2^{2+}$ reaches measurable concentrations. The other oxime complexes M(HL)$_2^{2+}$ are so stable and the mono complexes M(HL)$_2^{2+}$ so weak acids that they do not deprotonate to ML$^+$ before they disappear in the increase of pH.

Pyridine-2-carboxamidoxime forms Zn$_2$L$_2$OH$^+$ and Zn$_4$(L−H)$_2$L$_2^{2+}$ in the pH range 7–8. Apparently, their parent complex is Zn$_2$L$_2^{2+}$, which immediately forms a hydroxo bridge or polymerizes to the tetramer via amido $\text{−NH}−$ and oximato $\text{−NO}−$ bridges. Cadmium(II) ion forms similarly Cd$_4$(L−H)$_2$L$_2^{2+}$ in the pH range 8–10, but not Cd$_2$L$_2$OH$^+$. The larger size of cadmium(II) ion weakens especially the Cd−O bonds. The $d^{10}$ electron structures of zinc(II) and cadmium(II) favor coordination to nitrogen over the oxygen.

Pyridine-2-carboxamidoxime forms in the low pH range a binuclear complex Co$_2$(HL)$_2$H$_2$L$_5^+$, where one of the ligands is positively charged. The structure of the dimer is very difficult to predict. The deprotonation of the ligand H$_2$L$^+$ to HL in the pH range 2–3 causes decomposing of Co$_2$(HL)$_2$H$_2$L$_5^+$ to Co(HL)$_2^{2+}$ an Co(HL)$_2^{2+}$. Cobalt(II) ion forms also a complex Co(H$_2$L)$_3^+$ with a positively charged pyridine-2-acetamidoxime H$_2$L$^+$. It deprotonates to Co(HL)$_2^{2+}$ in the pH range 4–5, where the proportion of Co(HL)$_2^{2+}$ is rather small. Apparently, the positively charged ligands H$_2$L$^+$ are coordinated to the cobalt(II) ion as monodentate ligand. Nickel(II) and zinc(II) ions do not form complexes with positively charged ligands. Apparently, nickel(II) ion displaces the protons in the pH range 2–3 and zinc(II) cannot form stable complexes with positively charged ligands.

Both pyridine-2-acetamidoxime and pyrazine-2-carboxamidoxime form only Zn(HL)$_2^{2+}$ and Zn$_2$L$_2$OH$^+$ with zinc(II) and only Cd(HL)$_2^{2+}$ and CdL$^+$ with cadmium(II). The aqua Zn$^{2+}$ ion precipitates as Zn(OH)$_2$ in the pH range 7.0–7.5, where the proportions of the Zn$_2$L$_2$OH$^+$ complexes are very small. Cd(OH)$_2$ starts to precipitate at (pH =) 8–9, where also the proportion of CdL$^+$ complexes are also very small.
It is obvious that the formation of polynuclear species originates from the weak stabilities of the mononuclear bis and tris complexes. Due to the Jahn–Teller distortion, copper(II) ion does not form tris complexes with bidentate oximes. For the same reason also the structure of Cu$_2$L$_2$OH$^+$ would be highly unstable. Pyridine-2-acetamidoxime forms Cu$_2$L$_2^{2+}$, but pyridine-2-aldoxime and its methylated derivatives form trinuclear species Cu$_3$L$_3$OH$^{2+}$ and Cu$_3$L$_3$O$^+$ (or Cu$_3$L$_3$(OH)$_2$$^+$).

Pyridine-2,6-dicarboxamidoxime H$_2$L is a tridentate ligand and forms more stable complexes Cu(H$_2$L)$_2^{2+}$ (log $\beta_{011} = 6.66$), Ni(H$_2$L)$_2^{2+}$ (5.67), and Ni(H$_2$L)$_2^{2+}$ (log $\beta_{012} = 11.31$, log $K_2 = 5.64$) than the bidentate oxime ligands HL. However, due to the Jahn–Teller distortion the stepwise stability constant log $K_2$ of Cu(H$_2$L)$_2^{2+}$ is only 3.53. The crystal structure of [Ni(HL)$_2$]$\cdot$4H$_2$O determined with X-ray diffraction shows that in NiH$_2$L$_2$ both ligands are in the form HL$^-$, but the structure of Cu(HL)$_2$ is not clear in CuH$_2$L$_2$. The structure of Cu(HL)$_2$L is also possible; because the Jahn–Teller distortion weakens also the acidity of the ligand coordinated on the $z$ axis of Cu(H$_2$L)$_2^{2+}$.

**REFERENCES**

36. Stability Constants Database and Mini-SC Database, IUPAC and Academic Software, Version 5.3, Sourby Old Farm, Timble Otley, Yorks, UK, 2011 scbase@acadsoft.co.uk.
88
