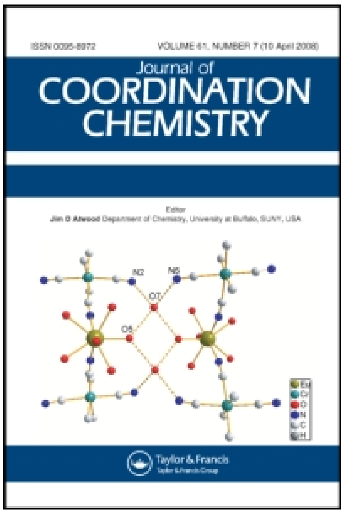

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Formation of zinc(II) and cadmium(II) complexes with pyridine-2-carboxamidoxime and pyridine-2-acetamidoxime in aqueous solution

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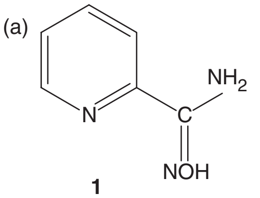
Complex formation equilibria of zinc(II) and cadmium(II) with pyridine-2-carboxamidoxime (**1**) and pyridine-2-acetamidoxime (**2**), HL, were studied in aqueous 0.1 $\mathrm{mol\,L^{-1}}$ NaCl solution at 25°C by potentiometric titrations with the use of a glass electrode. Experimental data were analysed with the least-squares computer program SUPERQUAD to determine the complexes formed and their stability constants. With ligand **1**, both metal ions formed mononuclear complexes $M(HL)^{2+}$, $M(HL)_2^{2+}$, $M(HL)L^{+}$, and ML_2 plus a tetranuclear species $M_4(L-H)_2L_2^{2+}$ through four oximato and two amido bridges. Additionally, a ternary binuclear complex $Zn_2L_2OH^{+}$ and a deprotonated mono complex CdL^{+} were formed. With ligand **2**, only $Zn(HL)^{2+}$, $Zn_2L_2OH^{+}$, $Cd(HL)^{2+}$, and CdL^{+} were found. The larger size of cadmium(II) ion markedly weakens its ability to form polynuclear complexes.

Keywords: Pyridine-2-amidoximes; Zinc(II); Cadmium(II); Complexes; Equilibria

1. Introduction

In an earlier paper, we described the complexation of divalent zinc and cadmium with pyridine-2-carboxaldehyde oxime (pyridine-2-aldoxime) and its methyl-substituted derivatives, 1-(2-pyridinyl)ethanone oxime and 6-methylpyridine-2-carboxaldehyde oxime [1]. In this article, the studies are extended to the following pyridine-2-amidoxime ligands: pyridine-2-carboxamidoxime (**1**) and pyridine-2-acetamidoxime (**2**). We earlier reported complex formation constants for all five pyridine-2-oximes with divalent copper [2, 3], nickel [2, 4, 5], and cobalt [6] ions. The series is now extended to **1** and **2** with divalent zinc and cadmium ions.



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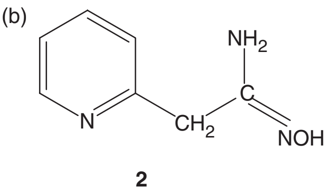

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Zinc(II) and cadmium(II) along with pyridine-2-aldoxime and 1-(2-pyridinyl)ethoxime form mononuclear complexes $M(HL)^{2+}$, $M(HL)_2^{2+}$, $M(HL)L^+$, ML_2, and *via* oximato and hydroxo bridges binuclear complexes $M_2L_2^{2+}$, $M_2L_2OH^+$, and $M_2L_2(OH)_2$ [1]. With 6-methylpyridine-2-aldoxime, only binuclear zinc(II) complexes and cadmium(II) complexes CdL^+, CdL_2, and $Cd_2L_2OH^+$ were observed [1]. Both metal(II) ions have d^{10} electronic structures, which is the reason for many properties of the soft Lewis acids. Cadmium(II) is clearly a soft Lewis acid, which more readily binds uncharged nitrogen donors than negatively-charged oxygen through electrostatic bonds [7]. The smaller zinc(II) has more properties of hard Lewis acids, more readily binding charged donors through electrostatic forces. The pyridine-2-aldoxime complex $Cd(HL)^{2+}$ due to π-bonds is more stable than the $Zn(HL)^{2+}$ complex, but other cadmium(II) complexes formed by these oximes, especially binuclear complexes, are less stable than the corresponding zinc(II) complexes. In all three systems, ZnL^+ are so readily dimerized to $Zn_2L_2^{2+}$ that only the pyridine-2-aldoxime complex ZnL^+ could be observed; CdL^+ could be observed in all three systems.

Ligand **1** forms only mononuclear copper(II) and nickel(II) complexes, which are more stable than the corresponding complexes with the three oximes above. Ligand **2** also forms the binuclear complexes $Cu_2L_2^{2+}$ and $Ni_2L_2OH^+$. However, the corresponding aminoamidoximes of the type $RR'N(CH_2)_nC(NH_2)NOH$ ($n = 1$ and 2) have a pronounced tendency to form stable tetra- and pentanuclear complexes *via* amido ($-NH^--$) and oximato ($-NO^--$) bridges [8–12]. Formation of polynuclear complexes seems to increase when the stabilities of bis (and tris) complexes decrease.

2. Experimental

2.1. *Reagents and solutions*

Pyridine-2-carboxamidoxime (**1**) and pyridine-2-acetamidoxime (**2**) were synthesized according to methods described in the literature [2]. Stock solutions of $ZnCl_2$ and $CdCl_2$ were standardized against ethylenediamine tetraacetic acid (EDTA).

2.2. *Potentiometric measurements and data treatment*

Investigation of the complex formation equilibria was carried out as a series of potentiometric titrations in aqueous 0.1 $mol\,L^{-1}$ NaCl solutions at 25.0°C. Due to poor solubility of some of the most interesting complexes in perchlorate solutions, NaCl was chosen as inert salt instead of the more common $NaClO_4$. The electrode system used in the measurements was described previously [9]. Before each titration, the potentiometer was recalibrated to hydrogen ion concentration, h, by the titration of 50 mL 0.1 $mol\,L^{-1}$ NaCl solution with 7 mL exactly known 0.1 $mol\,L^{-1}$ HCl solution, and known amount of metal ion and ligand was added to this solution. Ratios of the total concentrations of metal ion, C_M, to ligand, C_L, were held constant during measurements. Both forward (NaOH) and backward (HCl) titrations were performed to test the reproducibility and reversibility of the equilibria. The available concentration and $pH = -\log h$ ranges were defined by the formation of a precipitate or by very slow attainment of equilibrium.

In evaluating equilibrium constants, the binary two-component equilibria (1)–(4) were considered:

$$H^+ + HL \rightleftarrows H_2L^+;\ \beta_{101} \tag{1}$$

$$2H^+ + HL \rightleftarrows H_3L^{2+};\ \beta_{201} \tag{2}$$

$$HL \rightleftarrows H^+ + L^-;\ \beta_{-101} = K_a \tag{3}$$

$$pH^+ + qM^{2+} \rightleftarrows (H^+)_p(M^{2+})_q;\ \beta_{pq0} \tag{4}$$

These binary equilibria (1)–(4) have been studied previously. The values of the protonation constants of the pyridine nitrogen, $\log\beta_{101}$, and the values of the acid dissociation constants of the oxime group, pK_a, used in the calculations were 3.798 and 11.7 (ligand **1**) and 5.017 and 12.3 (ligand **2**), respectively [2]. For **2**, the second protonation constant, $\log\beta_{201} = 7.307$, was also used, but with **1** the weak protonation of the amide $-NH_2$ group did not enable an accurate determination of $\log\beta_{201}$ [2]. For binary hydrolytic equilibria of zinc(II), reaction (4), the values used, $\log\beta_{-110} = 9.15$ and $\log\beta_{-120} = -8.89$, were extrapolated from those determined in 2–3 mol L^{-1} NaCl and KCl solutions [13] to ionic strength 0.1 mol L^{-1} by Debye–Hückel-type equations established by Baes and Mesmer [14]. Chaberek *et al.* [15] ascertained the value of $\log\beta_{-110} = -11.6$ in 0.1 mol L^{-1} KCl at 30°C for cadmium(II). In this study, the used value of $\log\beta_{-110} = -11.8$ at 25°C was calculated by using the hydrolytic reaction enthalpy $\Delta H_{-110} = +54.8\ \mathrm{kJ\,mol^{-1}}$ determined by Arnek and Kakolowicz [16]. For cadmium(II), the values of $\log\beta_{-120} = -9.13$ and $\log\beta_{-440} = -32.37$ [14] were also used, extrapolated from the experimental values determined in 3 mol L^{-1} $LiClO_4$ solution by Biedermann and Ciavatta [17]. Metal hydrolysis was found to be negligible under our conditions.

The acid strengths of the oxime groups are very weak; so the corresponding pK_a values in reaction (3) 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:

$$pH^+ + qM^{2+} + rHL \rightleftarrows (H^+)_p(M^{2+})_q(HL)_r;\ \beta_{pqr}. \tag{5}$$

Mathematical analysis of data was performed with the least-squares computer program SUPERQUAD [18]. The p, q, r triplets and the corresponding equilibrium constants that best fit the experimental data were determined by minimizing the error sum $U = 3w_i(E_i^{obs} - E_i^{calcd})^2$. The weighting factor w_i is defined by the equation $w_i = 1/(\sigma_E^2 + \delta E_i/\delta V_i)\sigma_V^2$, where σ_E (0.1 mV) and σ_V (0.02 mL) are the estimated uncertainties in the electrode and titrant (NaOH) volume readings and $\delta E_i/\delta V_i$ is the slope of the titration curve. The criteria for choosing the best fit to the experimental data were χ^2 statistics and the sample standard deviation, s [19].

3. Results and discussion

To visualize the experimental results for zinc(II) and cadmium (II) complexation sets, Z_H *versus* pH were calculated. These plots are shown in figure 1. Z_H is defined

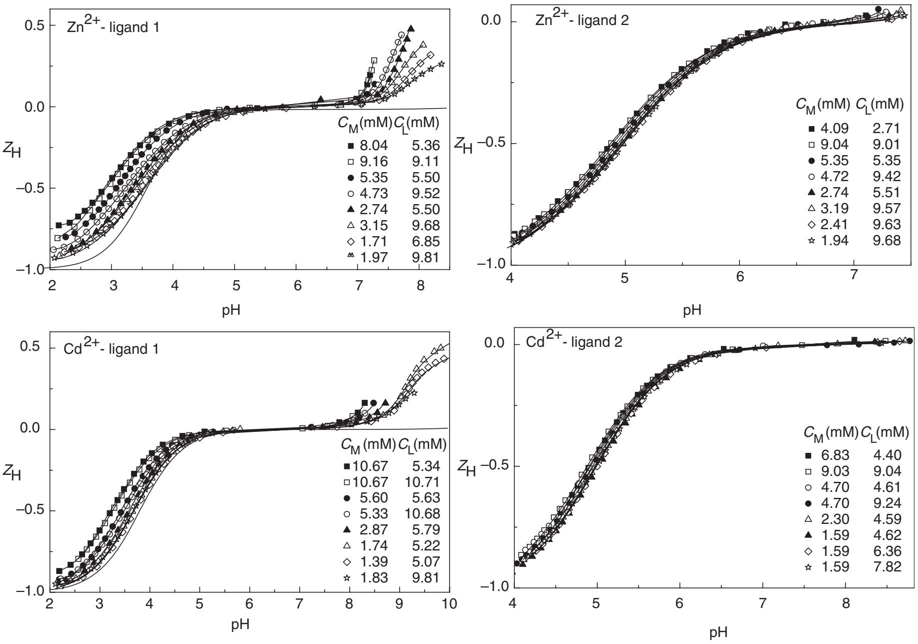

Figure 1. Part of the experimental data plotted as curves Z_H *vs.* pH. The full lines have been calculated using the sets of proposed stability constants in table 1. The lowest lines refer to the ligands alone.

as the average number of OH^- ions reacted per ligand (HL) and is given by the relation:

$$Z_H = \frac{h - C_H - K_w h^{-1}}{C_L}, \tag{6}$$

where C_H denotes the total concentration of hydrogen ions calculated over the zero level HL, H_2O, and M^{2+} [20, 21]. The formation of complexes causes dispersion to the curves from the curve of the ligand alone. The plateaus of the Z_H curves in the zero level indicate that there are only complexes of type $M(HL)_r^{2+}$ ($r = 0, 1, 2, \ldots$) and HL in the solutions. When the Z_H curves of the titrated solutions exceed the zero level, it implies the presence of some deprotonated complexes, for example $M(HL)L^+$ or L^-. To describe the differences between the experimental and calculated data sets, Z_H were also calculated using the stability constants and the values of h, pH, $[M^{2+}]$, and [HL] calculated by SUPERQUAD in equations (6) and (7).

$$\begin{aligned} C_H = h &+ (2\beta_{201}h^2 + \beta_{101}h - \beta_{-101}h^{-1})[HL] \\ &+ \Sigma p\beta_{pqr}h^p[M^{2+}]^q[HL]^r - K_w h^{-1}. \end{aligned} \tag{7}$$

3.1. *The Zn^{2+}–ligand 1 system*

The highest usable pH values in the SUPERQUAD calculations increased from 7.0 to 8.4 with the increase of the $C_L:C_M$ ratio. The model of mono and bis complexes

Table 1. Proposed structural formulas and stability constants ($\log\beta \pm 3\sigma$) for the reaction $p\mathrm{H}^+ + q\mathrm{M}^{2+} + r\mathrm{HL} \rightleftarrows (\mathrm{H}^+)_p(\mathrm{M}^{2+})_q(\mathrm{HL})_r$ in aqueous 0.1 mol L^{-1} NaCl solution at 25°C.

	p	q	r	Proposed formula	Log $\beta \pm 3\sigma$	Proposed formula	Log $\beta \pm 3\sigma$
Ligand **1**	0	1	1	$Zn(HL)^{2+}$	3.03 ± 0.02	$Cd(HL)^{2+}$	2.53 ± 0.01
	−1	1	1			CdL^+	-6.53 ± 0.07
	0	1	2	$Zn(HL)_2^{2+}$	5.47 ± 0.03	$Cd\,(HL)_2^{2+}$	4.17 ± 0.07
	−1	1	2	$Zn(HL)L^+$	-2.33 ± 0.08	$Cd(HL)L^+$	-4.28 ± 0.15
	−2	1	2	ZnL_2	-10.96 ± 0.23	CdL_2	-13.44 ± 0.08
	−3	2	2	$Zn_2L_2OH^+$	-14.32 ± 0.22		
	−6	4	4	$Zn_4L_2(L-H)_2^{2+}$	-24.96 ± 0.13	$Cd_4L_2(L-H)_2^{2+}$	-34.48 ± 0.17
	1	0	1	H_2L^+	3.798 ± 0.006		
	−1	0	1	L^-	-11.7		
Ligand **2**	0	1	1	$Zn(HL)^{2+}$	1.79 ± 0.02	$Cd(HL)^{2+}$	1.72 ± 0.02
	−1	1	1			CdL^+	-8.05 ± 0.11
	−3	2	2	$Zn_2L_2OH^+$	-16.29 ± 0.05		
	1	0	1	H_2L^+	5.017 ± 0.003		
	2	0	1	H_3L^{2+}	7.307 ± 0.013		
	−1	0	1	L^-	-12.3		
	−1	1	0	$ZnOH^{2+}$	-9.15[a]	$CdOH^{2+}$	-11.8[b]
	−2	1	0	Zn_2OH^{3+}	-8.89[a]	Cd_2OH^{3+}	-9.13[c]
	−4	4	0			$Cd_4(OH)_4^{4+}$	-32.37[c]

The protonation constants of the ligands are from Ref. [2].

[a] Extrapolated values from 2–3 mol L^{-1} NaCl and KCl solutions [13, 14].

[b] Calculated from the value of −11.6 in 0.1 mol L^{-1} KCl at 30°C [15] by using the hydrolytic reaction enthalpy $\Delta H_{-110} = +54.8$ kJ mol^{-1} [16].

[c] Extrapolated values from 3 mol L^{-1} $LiClO_4$ solution [14, 17].

with oximato and hydroxo bridged binuclear complexes $Zn_2L_2^{2+}$, $Zn_2L_2OH^+$, and $Zn_2L_2(OH)_2$ observed with pyridine-2-aldoxime and its methylated substituents proved unsatisfactory ($\chi^2 = 44.6$ and $s = 2.99$) with pyridine-2-carboxamidoxime. Addition of a tetranuclear species with the p, q, r combination −6,4,4 to the model gave a considerably better fit to the data. A plausible formula for the tetramer is $Zn_4(L-H)_2L_2^{2+}$, where two of the amide ($-NH_2$) groups are deprotonated and involved in coordination in the form of the amido $-NH^-$– anion. We earlier proved such a square-planar structure using X-ray analysis for the solid 2-(*N*-dialkylamino)acetamidoxime complexes in $[Cu_4(L\text{–}H)_2L_2](ClO_4)_2(H_2O)$ [8, 9]. Nickel(II) ions also form tetranuclear complexes $Ni_4(L-H)_2L_2^{2+}$ in aqueous solution [8, 9], but the green–brown color of the solutions suggest octahedral structures. Some binuclear species $Zn_2L_2^{2+}$ or $Zn_2L_2OH^+$, but not $Zn_2L_2(OH)_2$, also seem to form in the pH range 7–8. In this pH range, the hydrolyzed species $Zn_2L_2OH^+$ is more probable.

The final calculation, encompassing 379 points from eight titrations, without $Zn_2L_2(OH)_2$ selected $Zn_2L_2OH^+$ with $\chi^2 = 15.5$ and $s = 2.15$. The stability constants of the complexes are given in table 1. None of the additional polynuclear complexes tested in subsequent calculations made any significant contribution to the complex model. An example of the concentration distribution of the species is shown in figure 2. These calculations utilized the SPE computer program [22].

The Z_H curves of the system Zn^{2+}– **1** with $C_L : C_M = 3$–5 (figure 1) have a weak inflection point at *ca* $C_H = -C_M$ in the pH range 7.8–8.0. Around these points, $Zn(HL)L^+$ with $p = -q$ reaches its maximum concentration (only 20–30% of C_M) and the curves of $Zn(HL)^{2+}$ and $Zn(HL)_2^{2+}$ intersect the curves of $Zn_2L_2OH^+$ and

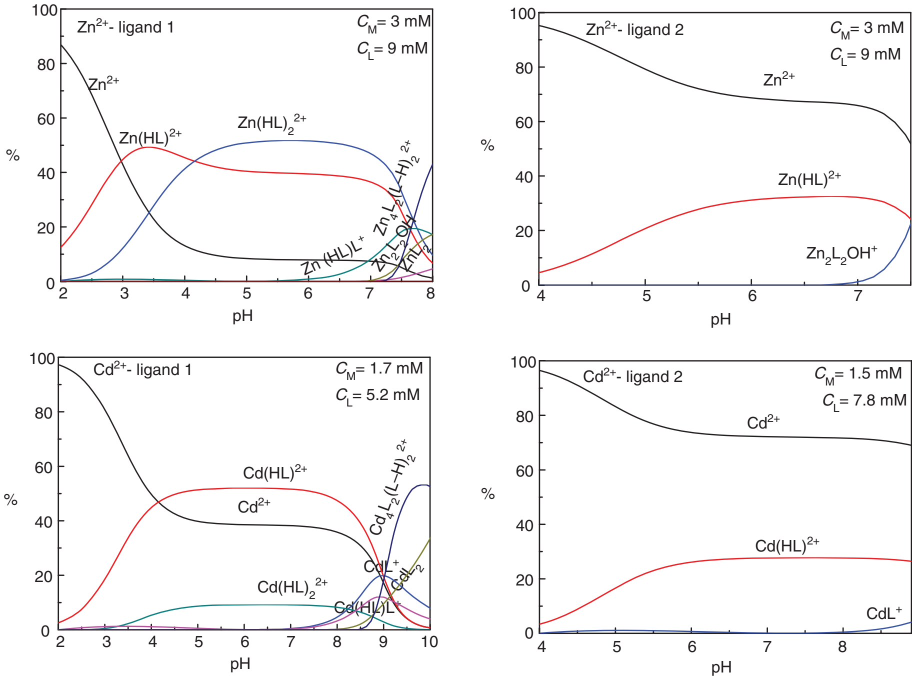

Figure 2. Examples of the concentration distributions of zinc(II) and cadmium(II) species *vs*. pH for **1** and **2**.

$Zn_4(L-H)_2L_2^{2+}$ so that the average $p=-q$. In the higher pH range, the major species is $Zn_4(L-H)_2L_2^{2+}$. In solutions of lower values of $C_L:C_M$ ratio, large amounts of uncomplexed Zn^{2+} ion are present in the pH range 7.0–7.3, where it precipitates as $Zn(OH)_2$. The solubility product of the amorphous $Zn(OH)_2$ at 25°C is 14.70 in $0.2\,\mathrm{mol\,L^{-1}}$ KNO_3 and $NaClO_4$ solution and 15.52 in pure water [23].

3.2. *The Cd^{2+}–ligand 1 system*

The titrations of this system could be continued to pH range 8–10 because the hydrolysis constant of Cd^{2+} ($\log\beta_{-110}=-11.8$) is two log units lower than the Zn^{2+} hydrolysis constant (−9.15). The Z_H curves with $C_L:C_M=3$–4 show no plateau or infection point above the zero level, but their $C_H:C_M$ ratios around pH = 10 exceed the value of −1.5 and seemingly approach −2.

SUPERQUAD calculations proved that the cadmium(II) complexes are less stable and undergo less polymerization in comparison to zinc(II) complexes. In the best fit to the experimental data ($\chi^2=48.6$, $s=1.44$, 400 points from eight titrations), the SUPERQUAD program rejected the binuclear complex $Cd_2L_2OH^+$ and calculated the stability constant of CdL^+. The stability constants are given in table 1. Particularly, the tetranuclear complex $Cd_4(L-H)_2L_2^{2+}$ is clearly less stable than $Zn_4(L-H)_2L_2^{2+}$. An example of the concentration distribution of the species is shown in figure 2. It shows that $Cd_4(L-H)_2L_2^{2+}$ is the major species in the pH range 9–10, but CdL_2 seems to displace it with further pH increase.

3.3. *The Zn^{2+}–ligand 2 system*

The slight dispersion of the Z_H curves (figure 1) demonstrates only weak complex formation in the pH range 4–7 while some deprotonated complexes are formed in the pH range 7.0–7.5, where the Z_H curves exceed the zero level. Ligand **2** is a weak acid ($pK_a = 12.3$) and only forms weakly acidic complexes, for example $Ni(HL)_2^{2+}$ with $pK_{a1} = 8.42$ [2]. Consequently, in pH range 7.0–7.5, where the concentration of $Zn(HL)^{2+}$ is low and $Zn(HL)_2^{2+}$ is absent, mononuclear deprotonated complexes such as ZnL^+ or $Zn(HL)L^+$ are improbable. The best fit to the experimental data ($\chi^2 = 11.7$, $s = 1.47$, 255 points from eight titrations) was obtained by assuming only the complexes $Zn(HL)^{2+}$ and $Zn_2L_2OH^+$ with the stability constant given in table 1. An example of the concentration distribution of the species is shown in figure 2.

3.4. *The Cd^{2+}–ligand 2 system*

After neutralization of the added HCl, the pH values of the solutions arose rapidly from range 6–7 to 8–9, where only 1–3 titration points were available in the SUPERQUAD calculation. This and the weak dispersion of the Z_H curves (figure 1) prove only weak complex formation also in this system. The best fit to these data from eight titrations and 230 points was obtained with a simple model of two species $Cd(HL)^{2+}$ and CdL^+ ($\chi^2 = 39.7$, $s = 1.11$) with the stability constants given in table 1. Although, the portion of the minor species CdL^+ was small in all the solutions (figure 2), it was accepted because it would be very difficult to find reasons to exclude the deprotonation of the parent complex $Cd(HL)^{2+}$ in the pH range 8.0–8.8. With **2** $Cd(HL)^{2+}$ is ($pK_a = 9.77$), as expected, about 0.7 pK_a units weaker acid than with **1** (9.06). Similar to this is the acidity difference between the $Ni(HL)_2^{2+}$ complexes with **2** ($pK_{a1} = 8.42$) and **1** (7.76) [2]. The small amounts of CdL^+ explain the slight exceeding of the Z_H curves above the zero level before the end of the titrations.

3.5. *Discussion*

Ligand **1** forms more stable but less acidic mononuclear zinc(II) and cadmium(II) complexes $M(HL)^{2+}$ and $M(HL)_2^{2+}$ than the pyridine-2-aldoxime and 1-(2-pyridinyl)ethanone oxime do [1]. The acidity of the oxime NOH group of the free ligand clearly affects the acidity of the formed complex. Pyridine-2-aldoxime ($pK_a = 10.01$), 1-(2-pyridinyl)ethanone oxime (10.87), and 6-methylpyridine-2-aldoxime (9.94) [3] form in the pH range 6–7 deprotonated binuclear complexes $Zn_2L_2^{2+}$, which deprotonate with $pK_a = 6.31$–6.83 in the increase of pH to $Zn_2L_2OH^+$ and further to $Zn_2L_2(OH)_2$ [1]. The complexes $Zn_2L_2^{2+}$ are probably formed through deprotonation of two $Zn(HL)^{2+}$ complexes and subsequent dimerization *via* two oximato $–NO^-–$ bridges forming a six-membered $(ZnNO)_2$ ring. The weakly acidic **1** ($pK_a = 11.7$) does not form such complexes until pH = 7.0–7.5, where the formed $Zn_2L_2^{2+}$ is immediately deprotonated to $Zn_2L_2OH^+$ or polymerized further to $Zn_4L_2(L-H)_2^{2+}$ *via* amido $–NH^-–$ and oximato $–NO^-–$ bridges. Also the deprotonated mononuclear bis complexes $Zn(HL)L^+$ and $Cd(HL)L^+$ appear with **1** in clearly higher pH ranges than with pyridine-2-aldoxime and 1-(2-pyridinyl)ethanone oxime. A sufficient excess of **1** ($C_L : C_M > 2$) is necessary to avoid precipitation of $Zn(OH)_2$ and $Cd(OH)_2$ in the pH ranges 7.0–7.5 and 8.0–8.5, respectively.

The structures of $Zn(HL)L^+$ and $Cd(HL)L^+$ are clear from several studies on similar compounds. Both these complexes contain an intramolecular hydrogen bridge =N–O–H···O–N= between the oxygens of the adjacent *cis*-oriented oxime groups [8, 24].

Since we have not been successful in our attempts to prepare a suitable crystal of the tetranuclear compound for X-ray analysis, the structures of $Zn_4L_2(L-H)_2^{2+}$ and $Cd_4L_2(L-H)_2^{2+}$ with oximato $-NO^-$– and amido $-NH^-$– bridges are only suggested on the basis of the similar structures of 2-(dialkylamino)acetamidoxime complexes formed with copper(II) [8, 9] and nickel(II) [8, 10]. The connection often found between the composition of the ternary hydrolytic complexes and binary hydroxo species $Cu_2(OH)_2^{2+}$, $Ni_4(OH)_4^{2+}$, and $Cd_4(OH)_4^{4+}$ of the metal ions [25–30] would suggest competing amidoximato complexes with structures $Cu_4(OH)_2L_4^{2+}$, $Ni_4(OH)_4(HL)_2L_2^{2+}$, and $Cd_4(OH)_4(HL)_2L_2^{2+}$ in aqueous solution, but for zinc(II) complexes such structures are improbable. The binary hydrolysis of zinc(II) produces only $ZnOH^+$ and Zn_2OH^{3+} before precipitation commences in the neutral region [13, 14]. Both zinc(II) [28] and cadmium(II) [30] mainly form binary complexes ZnL_n^{2+} and CdL_n^{2+} ($n = 1$–4) with imidazole (L) and only at low $C_L : C_M$ ratios also form in small amounts of ternary complexes $Zn(OH)L_n^{3+}$ ($n = 1$ or 3), $Zn_2(OH)L_n^{3+}$ ($n = 2$ or 3), and $Cd(OH)L^+$. The d^{10} electron structures of zinc(II) and cadmium(II) favor coordination to nitrogen over the oxygen. So the tetranuclear complex $Zn_4L_2(L-H)_2^{2+}$ becomes the major species in the pH range 7.5–8.0 (figure 2). The portions of the competing species $Zn_2L_2OH^+$ and ZnL_2 in the same pH range remain smaller. This is reflected as relatively large inaccuracies in the values of $\log\beta_{-322}$ and $\log\beta_{-212}$. The proposed structure of $Zn_4L_2(L-H)_2^{2+}$ is shown in figure 3.

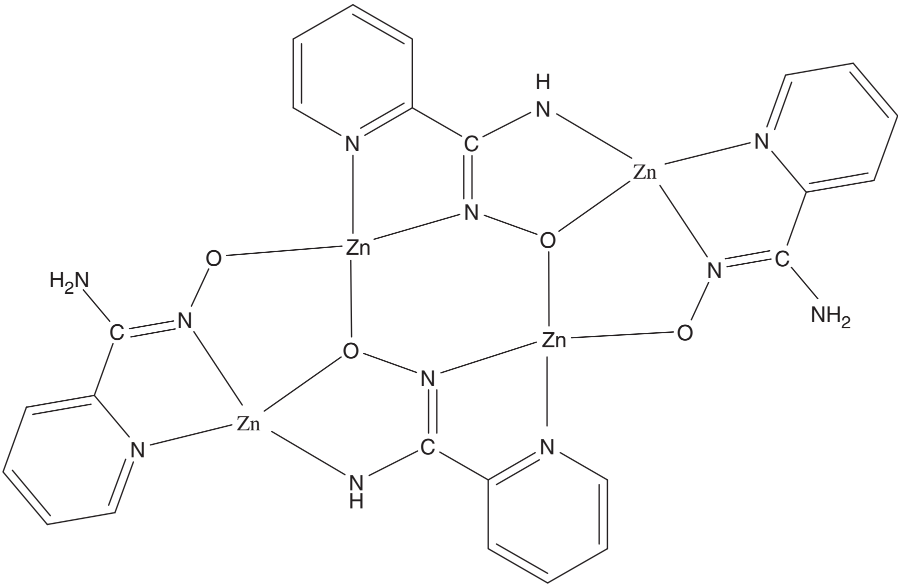

Figure 3. A proposed schematic representation for the tetranuclear complex ion $[Zn_4(L–H)_2L_2]^{2+}$ (HL = **1**) projected on a plane. Possible aqua ligands have been omitted.

The larger size of cadmium(II) weakens especially the Cd–O bonds and in this way the polymerization of CdL^+. For this reason, the $(CdNO)_2$ ring is much weaker than the $(ZnNO)_2$ ring. The tetramer $Cd_4(L-H)_2^{2+}$ is probably formed similar to $Zn_4(L-H)_2^{2+}$, but in the higher pH range 8.5–9.0 where the amido bridges outnumber the hydroxo bridges. Although $Cd_4(L-H)_2L_2^{2+}$ is the major species in the pH range 9–10, CdL^+ and CdL_2 are remarkable competing species (figure 2). In the further increase of pH, the tetranuclear species is seemingly displaced by CdL_2.

Weak complex formation of **2** with zinc(II) and cadmium(II) is due to the six-membered chelate rings, which are less stable than five-membered rings. Also, the oxime NOH group of **2** is weakly acidic ($pK_a = 12.3$), and the binuclear complex $Zn_2L_2OH^+$ with two oximato bridges and a hydroxo bridge is formed in the pH range 7.0–7.5, where the uncomplexed Zn^{2+} precipitates as $Zn(OH)_2$. CdL^+ is formed in a clearly higher pH range 8–9 because its oximate oxygen cannot coordinate to metal. The alternative binuclear structure $Zn_2(L\text{–}H)L^+$ or $Zn(L\text{–}H)ZnL^+$ with an uncoordinated oximate oxygen in L^- can be excluded in the pH range 7.0–7.5 also in the case of **1**. The hydroxides are precipitated soon after formation of $Zn_2L_2OH^+$ and CdL^+, and possible tetra- or pentanuclear complexes cannot be observed with **2**.

4. Conclusions

By comparing the results with those obtained previously, the stability of the mono complexes $M(HL)^{2+}$ increases with few exceptions in the orders 6-methylpyridine-2-aldoxime < **2** < pyridine-2-aldoxime < 1-(2-pyridinyl)ethanone oxime < **1** and $Cd^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$ [1–6]. Zinc(II) and cadmium(II) form bis complexes only with the three last-mentioned oximes, but copper(II), nickel(II), and cobalt(II) form also with **2** and 6-methylpyridine-2-carboxaldoxime bis complexes stabilized by ligand field.

Apparently, due to the weak acidities of the oxime NOH groups of **1** ($pK_a = 11.7$) and **2** ($pK_a = 12.3$), the formation of deprotonated complexes is insufficient to prevent precipitation of $Zn(OH)_2$ in the pH range 7–8 and the $Cd(OH)_2$ in the pH range 8–9 (figure 1). Especially with **2**, the deprotonated complexes $Zn_2L_2OH^+$ and CdL^+ appear just before precipitation of the hydroxides (figure 2). Instead, the more acidic 6-methylpyridine-2-aldoxime ($pK_a = 9.94$ [3]) forms in the presence of sufficient ligand excess without hydroxide precipitation, $Zn_2L_2^{2+}$, $Zn_2L_2OH^+$, and $Zn_2L_2(OH)_2$ in the pH range 6–8 and CdL^+, CdL_2, and $Cd_2L_2OH^+$ in the pH range 7–9, although $Zn(HL)^{2+}$ and $Cd(HL)^{2+}$ cannot be observed with this ligand [1].

The formation of polynuclear complexes obviously originates from the weak stability of the mononuclear bis (and tris) complexes. The polymerization of the complexes gives several alternative ways for the metal ions to complete their octahedral coordination spheres. The larger size of cadmium(II) weakens its ability to form polynuclear complexes *via* oximato bridges, and the deprotonated mono complex CdL^+ is observed also with **1** and **2**.

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