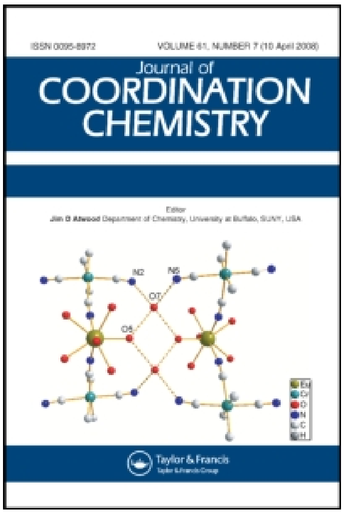

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FORMATION OF ZINC(II) AND CADMIUM(II) COMPLEXES WITH PYRIDINE OXIME LIGANDS IN AQUEOUS SOLUTION

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Complex formation equilibria involving pyridine-2-carboxaldehyde oxime (**1**), 1-(2-pyridinyl)ethanone oxime (**2**) and 6-methylpyridine-2-carboxaldehyde oxime (**3**), HL, with zinc(II) and cadmium(II) ions were studied in aqueous 0.1 M NaCl solution at 25° C by potentiometric titrations with a glass electrode. Experimental data were analysed with the least-squares computer program SUPERQUAD to determine the complexes formed and their stability constants. With Ligands **1** and **2** the sets of complexes for Zn(II) and Cd(II) are essentially the same, mono- and dinuclear oxime complexes and their deprotonated/hydrolysed products $H_pM_q(HL)_r^{2q+p}$. Owing to the steric requirements of the 6-methyl group, sets of complexes formed with **3** are distinctly different. For zinc(II), only dinuclear oximato species $H_pZn_2(HL)_2^{4+p}$ ($p = -2, -3, -4$) are found, while for the larger cadmium(II) ion mononuclear oximato species CdL^+ and CdL_2 are detected in addition to the dinuclear complex $H_pCd_2(HL)_2^{4+p}$ ($p = -3$).

Keywords: Pyridine oximes; Zinc(II); Cadmium(II); Complexes; Equilibria

INTRODUCTION

In earlier papers we described the complexation of pyridine-2-carboxaldehyde oxime, **1**, and its methyl substituted derivatives **2** and **3** with copper(II) [1], nickel(II) [2,3] and cobalt(II) [4] ions in aqueous solution. The set of mononuclear oxime complexes and their deprotonated/hydrolysed products $H_pM(HL)_r^{2+p}$ ($p = 0, -1, -2, -3$; $r = 1, 2, 3$) found in the various systems depends on the coordination tendency of the metal ion and the steric effect of the 6-methyl group. In addition to the mononuclear species, highly stable trinuclear complexes $Cu_3L_3OH^{2+}$ and $Cu_3L_3O^+$ containing a $Cu_3O(H)$ central core, have been verified for the three ligands in aqueous solution [1] and in the solid state [5, 6]. With the 6-methylated ligand **3** both di- and trinuclear complexes $Ni_2L_3^+$, $Ni_3L_3(OH)_2^+$, $Co_2L_2OH^+$, $Co_2L_3^+$ and Co_2L_3OH have been proposed. The studies have now been extended to include the aqueous complexation of zinc(II) and cadmium(II) with the pyridine oxime Ligands **1**–**3**.

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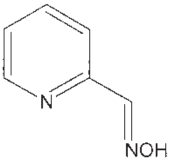

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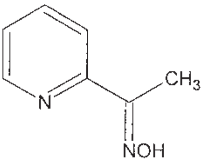

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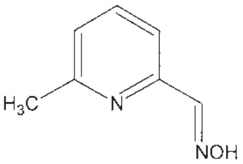

HL = **3**

EXPERIMENTAL

Reagents

Pyridine-2-carboxaldehyde oxime, **1** (99+%, Aldrich, gold label), was used without further purification. 1-(2-Pyridinyl)ethanone oxime, **2**, and 6-methylpyridine-2-carboxaldehyde oxime, **3**, were prepared according to literature methods [1]. Stock solutions of $ZnCl_2$ and $CdCl_2$ were standardized against EDTA.

Methods

Complex formation equilibria were studied in aqueous 0.1 M NaCl by potentiometric EMF measurements using a glass electrode. Because of the poor solubility of some of the most interesting complexes in perchlorate solutions, NaCl was used to control ionic strength instead of the more common $NaClO_4$. The electrode system used in the measurements and its calibration to hydrogen ion concentration, *h*, have been described earlier [7].

Ratios of the total concentrations of metal, C_M, to ligand, C_L, were held constant during the measurements. The available concentration and pH ($= -\log h$) ranges were defined by the formation of a precipitate or very slow attainment of equilibrium. Both forward (NaOH) and backward (HCl) titrations were performed to test the reproducibility and reversibility of the equilibria.

The binary two-component equilibria (1)–(3) were considered in evaluating the equilibrium constants:

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

$$HL \rightleftharpoons L^- + H^+; \qquad K_a \tag{2}$$

$$pH^+ + qM^{2+} \rightleftharpoons (H^+)_p(M^{2+})_q; \qquad \beta_{pq0} \tag{3}$$

The binary equilibria (1)–(3) have been studied earlier [1]. Values of protonation constants of the pyridine nitrogen, $\log\beta_{101}$, and of acid dissociation constants of the oxime group, pK_a, used in the calculations were 3.590 and 10.01 (ligand **1**), 3.968 and 10.87 (Ligand **2**) and 4.258 and 9.94 (Ligand **3**) [1]. For the binary hydrolytic equilibrium of reaction (3), we used the values $\log\beta_{110} = -9.15$ and $\log\beta_{210} = -8.89$ for zinc (II) and $\log\beta_{110} = -10.31$, $\log\beta_{210} = -9.13$ and $\log\beta_{-440} = -32.37$ for cadmium(II) [8].

The acid strengths of the oxime groups are very weak and thus the values of the corresponding pK_a values are not very accurate. This caused us, in evaluating the ternary equilibria, to choose the ligand as a component in the form of the uncharged oxime(HL):

$$p\mathrm{H}^+ + q\mathrm{M}^{2+} + r\mathrm{HL} \rightleftharpoons (\mathrm{H}^+)_p(\mathrm{M}^{2+})_q(\mathrm{HL})_r; \qquad \beta_{pqr} \tag{4}$$

The computer program SUPERQUAD [9] was used in the search of complex models (pqr) and corresponding stability constant β_{pqr}. The best fit to the experimental data was determined by minimizing the error square sum $U = \sum w_i(E_I^{\mathrm{obs}} - E_I^{\mathrm{calc}})^2$. The weighting factor w_i is defined by the equation $w_i = 1/(\sigma_{\mathrm{E}}^2 + \delta E_i/\delta V_i)\sigma_{\mathrm{V}}^2$, where $\sigma_{\mathrm{E}}(= 0.1\,\mathrm{mV})$ and $\sigma_{\mathrm{V}}(= 0.02\,\mathrm{mL})$ are the estimate uncertainties in the electrode and volume readings, and $\delta E_i/\delta V_i$ is the slope of the titration curve. As criteria in choosing the complex model that best describes the experimental data we used χ^2 statistics and the sample standard deviation s [10].

RESULTS AND DISCUSSION

Sets results of $\mathrm{Z_H}$ *versus* pH were calculated as a means of visualizing the experimental results. $\mathrm{Z_H}$ is defined as the average number of $\mathrm{OH^-}$ ions reacted per ligand (HL) and is given by the relation $\mathrm{Z_H} = (h - C_{\mathrm{H}} - k_w h^{-1})/C_{\mathrm{L}}$, where C_{H} denotes the total concentration of protons calculated over the zero level HL, $\mathrm{H_2O}$ and $\mathrm{M^{2+}}$. Figure 1 shows plots for zinc(II)–Ligand **2** and cadmium(II)–Ligand **2** titrations. The form of the plots was basically the same for all six metal–ligand systems and showed complexation to be accompanied by removal of oxime or aqua protons, or both. The $\mathrm{Z_H}$ value, which appears to approach 2 in the 1 : 1 titrations, further indicates that a limiting species $\mathrm{H}_{-2n}\mathrm{M}_n(\mathrm{HL})_n$ is formed in alkaline solutions.

The Ligand 1 Systems

With low $C_{\mathrm{L}}/C_{\mathrm{M}}$ ratios the upper pH ranges that could be used in the calculations were 7.0–7.5 for zinc(II) and 8.0–8.5 for cadmium(II). In general, excess ligand ($C_{\mathrm{L}} \gg C_{\mathrm{M}}$) extended the available pH range to 9–10.

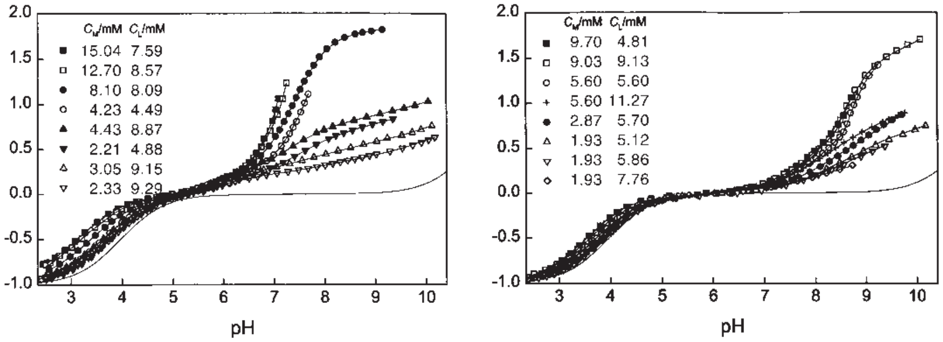

FIGURE 1 A portion of the experimental data plotted as curves $\mathrm{Z_H}$ *vs* pH for zinc(II) (left) and cadmium(II) (right) complex formation with Ligand **2**. The full lines have been calculated using the sets of proposed stability constants in Table I. The lowest lines refer to the ligand alone.

Titration curves of zinc(II) with $C_L/C_M = 2–4$ revealed a weak inflection point at *ca.* $C_H \approx -1.7\,C_M$. Although this may suggest the presence of a polynuclear species with $p/q = -5/3$, such as $Zn_3L_3O^+$ or $Zn_3L_3(OH)_2^+$, SUPERQUAD calculations led to much better χ^2 and s for a set of dinuclear complexes $H_pZn_2(HL)_2$ than for any single tri- or tetranuclear species.

The weak inflection points appeared in the pH range 8.0–8.4, where the major species are $Zn_2L_2OH^+$ and ZnL_2. It may be noted that the summation of $-3, 2, 2$ and $-2, 1, 2$ gives the same p/q ratio of $-5/3$. The analysis, based on 413 titration points from 8 titrations, terminated at $\chi^2 = 53.3$ and $s = 2.42$. This can be considered to provide a fairly good explanation of the data (s values lower than 3 are generally regarded as acceptable for comparable systems) [10]. The proposed complexes with their stability constants are given in Table I.

From the similar d^{10} electronic structures of cadmium(II) and zinc(II), one would expect the coordination of the two metals to be very similar. In the cadmium(II) systems, distinct inflection points can be verified in titration curves where ligand was used in excess. The best fit ($\chi^2 = 45.3$, $s = 1.89$; 465 data points from 8 titrations) was obtained by assuming a set of mono- and dinuclear complex species closely similar to the set proposed for zinc(II). The complexes and their stability constants are given in Table I.

With **1** there is some indication of the formation of tris complexes ZnL_3^- and CdL_3^- with high C_L/C_M ratios in the high pH range (pH > 8.5), but owing to the low concentrations of these complexes their presence could not be verified.

The Ligand 2 Systems

With zinc(II) the highest pH value used in the calculations was *ca.* 9.6. In general, the increase of ligand excess extended the available pH range to higher values.

TABLE I Stability constants and proposed formulae for pyridine oxime complexes with Zn^{2+} and Cd^{2+}

p, q, r	*Formula*	$\log\beta_{pqr}$		
		Ligand **1**	*Ligand* **2**	*Ligand* **3**
0 1 1	$Zn(HL)^{2+}$	1.902 ± 0.007	2.723 ± 0.05	
−1 1 1	ZnL^+	-4.81 ± 0.09		
0 1 2	$Zn(HL)_2^{2+}$		4.30 ± 0.05	
−1 1 2	$Zn(HL)L^+$	-2.50 ± 0.08	-0.860 ± 0.007	
−2 1 2	ZnL_2	-9.440 ± 0.013	-9.75 ± 0.05	
−2 2 2	ZnL_2^{2+}	-6.76 ± 0.09	-5.88 ± 0.02	-8.24 ± 0.08
−3 2 2	$Zn_2L_2OH^+$	-13.296 ± 0.014	-12.711 ± 0.011	-14.554 ± 0.012
−4 2 2	$ZnL_2(OH)_2^{2+}$	-22.66 ± 0.07	-20.697 ± 0.011	-22.84 ± 0.03
−3 1 3	ZnL_3^-	-17.09 ± 0.06		
0 1 1	$Cd(HL)^{2+}$	2.022 ± 0.006	2.370 ± 0.005	
−1 1 1	CdL^+	-5.26 ± 0.04	-5.558 ± 0.016	-5.714 ± 0.009
−1 1 2	$Cd(HL)L^+$	-2.97 ± 0.04	-2.921 ± 0.018	
−2 1 2	CdL_2	-10.933 ± 0.011	-11.724 ± 0.016	-11.486 ± 0.011
−2 2 2	CdL_2^{2+}	-8.02 ± 0.06		
−3 2 2	$Cd_2L_2OH^+$	-16.66 ± 0.03	-17.44 ± 0.04	-17.37 ± 0.02
−3 1 3	CdL_3^-	-18.35 ± 0.04		

The stability constants and formulae relate to the reaction $pH^+ + pM^{2+} + rHL \rightleftharpoons (H^+)_p(M^{2+})_q(HL)_r$.

With cadmium(II), a colorless precipitate appeared in the $C_L/C_M = 4$ titration at pH *ca.* 9.0 and in the $C_L/C_M = 3$ 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.

With zinc(II), a weak inflection point appeared in titrations at $C_H/C_M = -1$ where C_L/C_M was 3 and 4. In these two solutions the major species, $Zn(HL)L^+$, reached the maximum concentrations, 80 and 85% of C_M, respectively, around the inflection points, at $pH \approx 7.1$. In the higher pH range, ZnL_2 was replaced by $Zn_2L_2(OH)_2$ as major species. No tris complexes of Ligand **2** were observed under the experimental conditions used.

SUPERQUAD calculations gave the best χ^2 and s statistics for almost identical models of mono- and dinuclear complexes for zinc(II) ($\chi^2 = 25.2$, $s = 2.10$; 425 data points from 8 titrations) and cadmium(II) ($\chi^2 = 30.0$, $s = 2.35$; 456 data points from 8 titrations). The proposed complexes and their stability constants are given in Table I.

The Ligand 3 Systems

Complex formation involving **3** with zinc(II) and cadmium(II) ions was relatively weak and the complexes were considerably less stable than those of **1** and **2**. With low C_L/C_M ratios SUPERQUAD calculations showed high concentrations of uncomplexed aqua ions to be present in the solutions, even at the highest pH values used in the calculations. The following set of zinc(II) complexes was obtained: $Zn_2L_2^{2+}$, $Zn_2L_2OH^+$ and $Zn_2L_2(OH)_2$ ($\chi^2 = 53.6$, $s = 3.18$; 164 data points from 8 titrations). It may be noted that all mononuclear zinc(II) species were rejected during the calculation procedure when the dinuclear complexes were included. This is in contrast to the Cd^{2+}–**3** system, for which the following set of mono and dinuclear complexes was proposed: CdL^+, CdL_2 and $Cd_2L_2OH^+$ ($\chi^2 = 32.9$, $s = 2.72$; 253 data points from 8 titrations). Although the sample standard deviation s is somewhat high, it still indicates a satisfactory explanation of the data for both metals.

Discussion

Table I shows that the values of $\log\beta_{pqr}$ generally increase in the ligand order **3** < **1** < **2**. The same order was observed from copper(II), [1] nickel(II) [2, 3] and cobalt(II) [4]. The weaker tendency of **3** towards complex formation is apparently due to the steric requirements of the 6-methyl group. A similar weakening effect of 6- or 2-methyl groups on complex stability has been observed in comparable instances, for example with methylated pyridine [11] and pyridine-2-carboxylate ligands [12]. With large metal ions, such as Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^{2+} and Hg^{2+}, the increased basicity of the ligand caused by the presence of methyl group may actually lead to stabilization of the complexes. Such is the case, for example, with the 6-methyl-2-picolinate ligand [12].

Complexes of the type $M(HL)^{2+}$ formed with Ligand **2** were more stable than those formed with **1**. This is due to the stronger basicity of the pyridine nitrogen in **2**. The basicity of the oximate NO^- group is also stronger in **2** than in **1**. This affects the stabilities of the deprotonated oximato complex species formed with these two ligands. The values of the conventional stability constants calculated according to Eq. (5)

$$M^{2+} + rL^{-} \rightleftharpoons ML_r^{2-r}; \qquad \beta_r = K_a^r \beta_{pqr} \tag{5}$$

show Ligand **2** to form more stable mono and bis complexes CdL^+ and CdL_2 ($\log\beta_1 = 5.31$ and $\log\beta_2 = 10.02$) than does ligand **1** ($\log\beta_1 = 4.75$ and $\log\beta_2 = 9.09$). This is also true for the complex ZnL_2 ($\log\beta_2 = 11.99$ for Ligand **2** and $\log\beta_2 = 10.58$ for **1**).

Deprotonated bis complexes, $Zn(HL)L^+$ and $Cd(HL)L^+$, were found for Ligands **1** and **2**. It is clear that both these complexes contain an intramolecular hydrogen bridge $=N{-}O{-}H \cdots O{-}N=$ between the oxygen atoms of two adjacent oxime groups, as has been verified in several structures with comparable ligands [13,14]. Such a species was not detected for **3**, evidently because its 6-methyl groups cause steric interference with the cis orientation of the oxime groups [1, 2, 4].

The cadmium(II) complexes in Table I are usually less stable than the corresponding zinc(II) complexes. The exception, found in the mono complexes $M(HL)^{2+}$ with Ligand **1**, is not uncommon, however, and is regularly valid for ligands containing sulfur and phosphorus donor atoms and also for some systems with nitrogen donors [15]. Such ligands can be considered as soft Lewis bases, which preferably form π-bonds with soft Lewis acid, for example with uni- and bidentate metal ions having a d^{10} electronic structure [16]. The cadmium(II) ion can be characterized as a soft acid, but the smaller zinc(II) ion has properties of a hard Lewis acid.

The complexes $Zn_2L_2^{2+}$ are probably formed by dimerization of ZnL^+ complexes via two oximato NO bridges. In these dimerization reactions the metal atom of the complex ZnL^+ acts as a Lewis acid and the oximate oxygen atom of the ligand as a Lewis base. The oximate NO^- group of Ligand **2** is a stronger Brønstedt base than this group in **1**. With the stronger Brønstedt base, the species ZnL^+ with **2** is also a harder Lewis base, and so readily does it dimerize to $Zn_2L_2^{2+}$ that the monomer is not detected at all. With **1**, the dimerization of ZnL^+ to $Zn_2L_2^{2+}$ occurs to lesser extent, the maximum concentration of the monomeric species being *ca.* 15% of C_M.

With **2**, the dinuclear species $Zn_2L_2(OH)_2$ was stable enough to be the major species in the pH range 8–9, even in the presence of fourfold excess of total ligand. Distribution of the metal species at two C_L/C_M ratios is illustrated in Fig. 2. With **1** the situation is different: the concentration of the bis complex ZnL_2 may reach 80% of C_M at pH 9. The large amount of ZnL_2 in the solution made it possible to detect the formation of the tris complex ZnL_3^-, a species that has not been reported earlier [17,18].

Dimerization of CdL^+ was comparatively weak in all three systems and $Cd_2L_2^{2+}$ could be detected only with Ligand **1**. With **2** and **3** the dimerization, which occurred mainly when $pH > 7.5$, yielded the hydrolysed species $Cd_2L_2OH^+$. With **2**, small amounts of the more hydrolysed dimer $Cd_2L_2(OH)_2$ were found in the pH range 9–10, where the bis complex CdL_2 prevails as a major species in all three systems.

In the hydrolysed dimers $Zn_2L_2OH^+$ and $Cd_2L_2OH^+$, the metal ions probably have an octahedral coordination environment with a hydroxo and two oximato bridges between the central ions. A corresponding $Cu_2L_2OH^+$ structure would be highly unstable because of Jahn–Teller distortion. This probably explains why no dinuclear complexes have been found in the copper(II) systems, where polymerization leads to

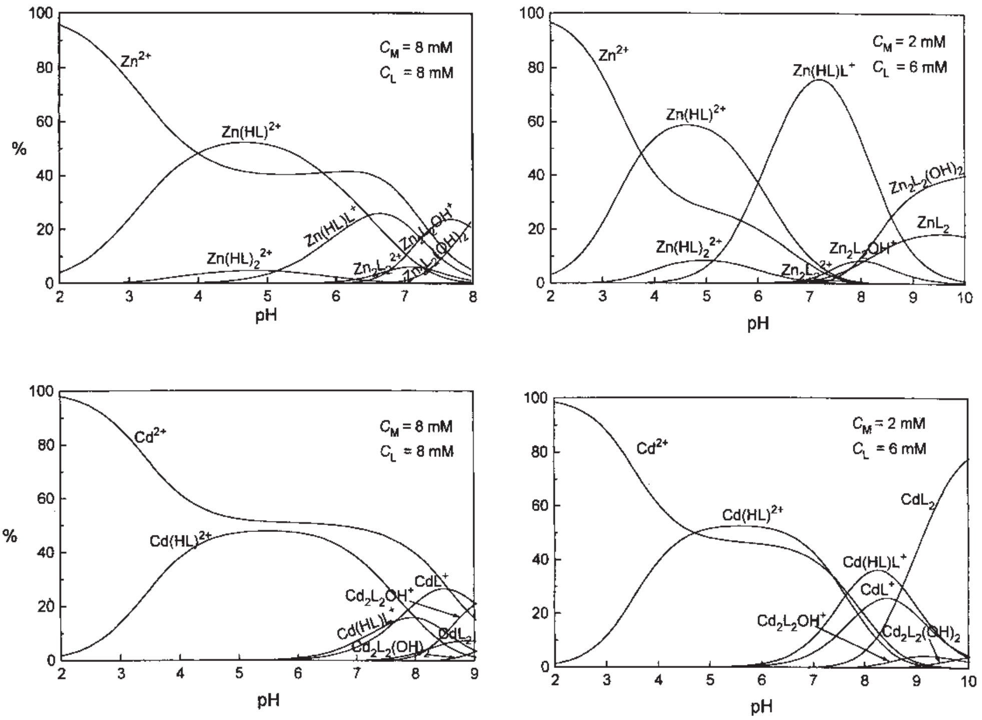

FIGURE 2 Examples of the concentration distributions of the zinc(II) and cadmium(II) species *vs* pH for Ligand **2**.

the formation of the trinuclear species $Cu_3L_3OH^+$ and $Cu_3L_3O^+$. In trinuclear copper(II) complexes, the $Cu_3O(H)$ core is held together by three peripheral oximato bridges [1, 6]. The oxygen atom in the core is located above the Cu_3 plane and thus exhibits a roughly tetrahedral coordination sphere [6,19].

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