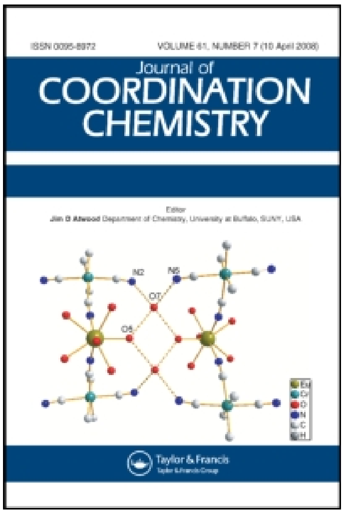

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FORMATION OF TRINUCLEAR COPPER(II) COMPLEXES WITH THREE PYRIDINE OXIME LIGANDS IN AQUEOUS SOLUTION

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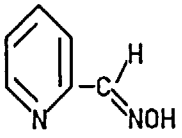
The protonation and complex formation equilibria of pyridine-2-carboxaldehyde oxime (1), 1-(2-pyridinyl)ethanone oxime (2) and 6-methylpyridine-2-carboxaldehyde oxime (3), HL, with copper(II) ion were studied in aqueous 0.1 M NaCl solution at 25°C by potentiometric titrations with the use of a glass electrode. Application of the least-squares computer program SUPERQUAD to the experimental data indicated that the following complex species are formed: $Cu(HL)^{2+}$, CuL^{+} (ligand 1), $Cu(HL)_2{}^{2+}$ (ligands 1 and 3), $Cu(HL)L^{+}$, CuL_2, $Cu_3L_3OH^{2+}$ and $Cu_3L_3O^{+}$ (or $Cu_3L_3(OH)_2{}^{+}$, ligands 1 and 2). The trinuclear complex $Cu_3L_3OH^{2+}$ most probably has a triangular Cu_3OH central core. In 1:1 molar ratio of ligand to Cu^{2+} the trimer exists as the predominating complex around pH 4–6 and gives way to the next deprotonated trimer as the pH is increased.

Keywords: Pyridine oximes, copper(II) complex, equilibria

INTRODUCTION

Bidentate oxime ligands with a nitrogen donor function two carbon atoms away from the oxime group have been found to possess a strong tendency to yield trinuclear copper(II) complexes.[1,2] A common feature of these structures is the presence of a triangular central Cu_3OH or Cu_3O core, which gives rise to the interesting electron transfer properties of the compounds.[3,4]

The aim of the present investigation was to interpret the aqueous complexation between copper(II) and pyridine-2-carboxaldehyde oxime, 1, and its methylated derivatives 2 and 3. Formation of trinuclear complexes can be expected with all three ligands. There are several earlier equilibrium studies of the aqueous Cu^{2+}-ligand 1 system.[5-10] Most authors do not, however, mention polynuclear complexes at all, while others propose the existence of several different di-, tri- and tetranuclear species. No stability constants of the polynuclear complexes have been given in these investigations.



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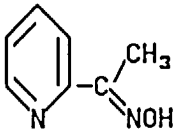

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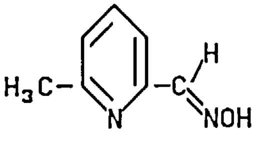

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Considering the inconsistencies in earlier interpretations and the basic importance of this system, reliable equilibrium analyses should be of great interest. In this study we have used as wide concentration ranges as possible so that the nature of the polynuclear complexes could be examined. This report is a part of our investigation of the structural and equilibrium characteristics of polynuclear copper and nickel complexes of oxime ligands.

EXPERIMENTAL

Pyridine-2-carboxaldehyde oxime, 1 (99+ %, Aldrich, gold label), was used without further purification.

1-(2-Pyridinyl)ethanone oxime, 2, was prepared by action of hydroxylamine on 1-(2-pyridinyl)ethanone. To a suspension of $NH_2OH.HCl$ (0.2 mol) and 1-(2-pyridinyl)ethanone (0.2 mol) in ethanol was added a sodium ethoxide solution (prepared by dissolving 0.2 mol of sodium in absolute ethanol). After removal of NaCl by filtration the solution was stirred 24 hours at 40°C. When treated with water, a white crystalline solid precipitated. Recrystallization two times from benzene. M.p. 121°C (lit.[11] 120°C).

6-Methylpyridine-2-carboxaldehyde oxime, 3, was prepared according to the method of Drago and Baucon.[12] A solution of 6-methylpyridine-2-carboxaldehyde (0.2 mol) in methanol was treated with a solution of hydroxylamine (prepared by adding a methanolic solution of $NH_2OH.HCl$ (0.22 mol) to an aqueous solution of NaOH (0.22 mol). After refluxing the mixture for several hours, a white crystalline solid was formed. Recrystallization was carried out twice from methanol. M.p. 170–171°C (lit.[13] 168–170°C).

The purity of the oxime ligands was checked by potentiometric titrations and DSC methods. The solution of $CuCl_2$ was standardized against standard EDTA and electrogravimetrically.

Methods

The investigation was carried out as a series of potentiometric titrations at 25°C at ionic strength 0.10 adjusted with sodium chloride. NaCl was chosen as the inert salt instead of $NaClO_4$ because of the poor solubility of some of the most interesting complex species in perchlorate solutions.

The free hydrogen ion concentration, h, was determined by measuring the emf of the cell $-\mathrm{RE}|$ equilibrium solution $|\mathrm{GE}+$ where GE denotes a glass electrode and RE = Hg, $Hg_2Cl_2|0.10\,M$ NaCl. Assuming the activity coefficients to be constant, the following expression is valid:

$$E = E_o + 59.157 \log h + E_j$$

For each separate run the electrode system was calibrated against the background electrolyte by means of E_o, E_j titration, after which the main run was started. For the liquid junction potential we used $E_j = j_h \cdot h$; the value of j_h varied slightly in different titrations, with the average value being $-480\,\mathrm{mV\,mol^{-1}\,dm^3}$.

During the measurements h was varied by adding hydroxide or hydrogen ions to the solution. The total concentrations of copper(II), C_M, and ligand, C_L, were varied within the limits $0.002 \leqslant C_M \leqslant 0.010$ M, $0.004 \leqslant C_L \leqslant 0.016$ M, covering the C_L/C_M ratios 1:2, 1:1, 1.5:1, 2:1, 4:1 and 8:1. The available pH range was determined by formation of a precipitate or very slow attainment of equilibria. In the different metal–ligand systems the upper pH values used in the equilibrium analyses were 7.6 (ligand **1**), 9.6 (ligand **2**) and 6.8 (ligand **3**).

Both forward (increasing pH) and backward (decreasing pH) titrations were performed to test the reproducibility and reversibility of the equilibria.

In evaluating the stability constants the two-component equilibria (*1–3*) and the three-component equilibrium (*4*) are the following when H^+, Cu^{2+} and the neutral oxime, HL, were chosen as components.

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

$$HL \leftrightharpoons L^- + H^+;\ k_a \tag{2}$$

$$pH^+ + qCu^{2+} \leftrightharpoons (H^+)_p(Cu^{2+})_q;\ \beta_{pqo} \tag{3}$$

$$pH^+ + qCu^{2+} + r(HL) \leftrightharpoons (H^+)_p(Cu^{2+})_q(HL)_r;\ \beta_{pqr} \tag{4}$$

For the binary hydrolytic equilibrium (*3*) we used the results summarized by Baes and Mesmer;[14] Cu^{2+} hydrolysis was found to be negligible in our conditions. No attention was paid to the possible formation of chloro complexes. In the evaluation of the three-component experimental data the binary complex models were considered as known and no attempts were made to adjust the corresponding equilibrium constants.

The mathematical analyses of the data were performed with the least-squares computer program SUPERQUAD.[15] The p,q,r triplets and corresponding equilibrium constants that best fit the experimental data were determined by minimizing the error squares sum

$$U = \Sigma w_i(E_i^{obs} - E_i^{calc})^2$$

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 volume readings, and $\delta E/\delta V$ is the slope of the titration curve.

RESULTS

The H^+-ligand systems

The values of the protonation constants, $\log\beta_{101}$, of the pyridine nitrogens and the values of the acid dissociation constants, pk_a, of the oxime groups of the different ligands are collected in Table I.

TABLE I

Values of the protonation constants of ligands **1–3** relating to the reactions (1)–(2).

Ligand	$\log(\beta_{101} \pm 3\sigma)$	$p(k_a \pm 10\sigma)$	No. of points/ titrations	χ^2	S
1	3.590±.005	10.01±.03	116/4	21.1	2.31
2	3.968±.003	10.87±.03	120/4	17.3	1.46
3	4.258±.008	9.94±.06	108/4	16.9	2.67

The effect of the methyl substitution on the proton–ligand equilibria was as expected. The 6-CH_3 group of **3** increases the basicity of the pyridine nitrogen, while the oxime group is not affected. With **2**, on the other hand, the acidity of the oxime group is considerably lowered by the adjacent CH_3 group and its effect on the pyridine nitrogen is not very marked.

Since the acidities of the oxime groups are very low it was necessary to obtain potential readings from relatively high pH ranges (values of pH up to 10.8 were used). Because of the reduced accuracy of the glass electrode under such alkaline conditions the pk_a values describing the oxime deprotonation cannot be regarded as very reliable. For this reason, very large error limits (10σ) were estimated for the corresponding constants in Table I.

The Cu^{2+}-ligand systems

Sets Z_H *versus* pH were calculated to visualize the experimental results for Cu^{2+}-ligand systems. Some of these plots are shown in Figure 1. Z_H is defined as the average number of OH^- ions reacted per ligand (HL) and is given by the relation $Z_H = (h - C_H - k_w h^{-1})\ C_L$, where C_H denotes the total concentration of protons calculated over the zero level HL, H_2O and Cu^{2+}.

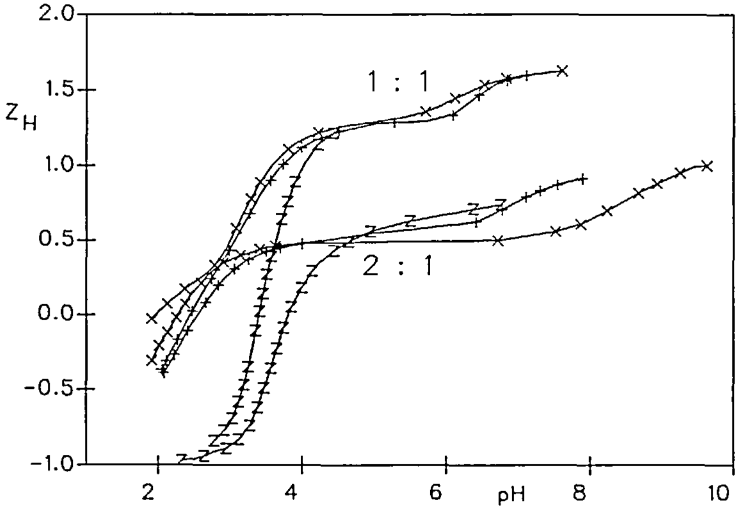


FIGURE 1 Parts of the experimental data plotted as curves of Z_H *vs* pH for C_L: C_M ratios 1 and 2. The symbols +, x and z refer to the ligands **1**, **2** and **3**, respectively. The full curves have been calculated using the values of stability constants in Tables 1 and 2.

In the titrations with $C_L/C_M = 1$ a plateau corresponding to $Z_H = 1.3$ appears near pH = 5 in all three systems. This implies that a predominating complex with *p,q,r* ratio of −4,3,3 is present. With ligands **1** and **2** where measurements can be carried out to higher pH than with **3**, Z_H seems to reach a limiting value of 1.7 in neutral or slightly acidic solution. This suggests that a species of the composition −5,3,3 is formed at the end of these titrations. In general, the finding of Z_H values greater than 1 in these plots directly demonstrates the formation of mixed hydroxo complexes with all these ligands.

Inspection of the $C_L/C_M = 2$ titrations shows a plateau for ligand **1** corresponding to $Z_H = 0.5$ and a limiting Z_H value of 1. These values point to the presence of predominating species with p,q,r ratios of $-1,1,2$ and $-2,1,2$, respectively. Data for the other ligands where pH ranges were narrower than for **1** do not readily reveal what complexes are formed. The presence of several simultaneously existing species is obvious.

It may be added that when the conventional Bjerrum plots, $n(\log[HL])$, are constructed no single curves independent of the total metal ion and ligand concentrations are found in any of the systems. Thus no additional information on the nature of the complexes or good estimates of the values of their stability constants can be obtained from this function.

In the computational analysis all mononuclear complexes $Cu(HL)_r(L)_s$ where $r+s \leqslant 2$, together with species having p,q,r ratios of $-4,3,3$ and $-5,3,3$, were tested against the whole data. This was done in SUPERQUAD[15] calculations in which the equilibrium constants of the proposed species were systematically varied. Compositions and formation constants of the complexes obtained are listed in Table II. The S and χ^2 values obtained in these calculations indicated a quite satisfactory fit to the experimental data. None of the additional di-, tri-, tetra- or hexanuclear complexes tested in subsequent calculations was found to make a significant contribution to the models. Thus we suggest the complexes and their formation constants given in Table II as a final result of the complexation under the conditions used.

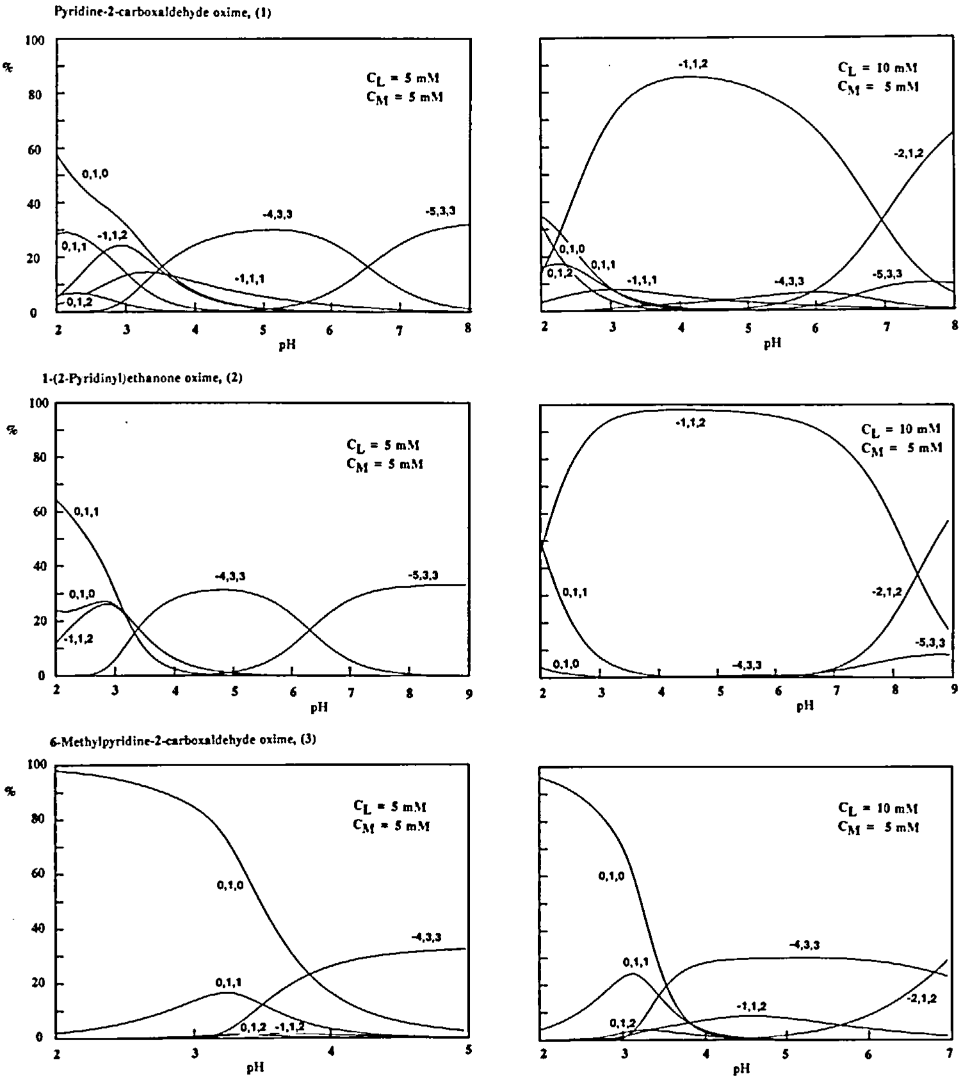
TABLE II

Stability constants for the pyridine oxime complexes with Cu(II) (25°C, $I = 0.1$ NaCl).

p,q,r	Proposed formula	$\text{Log}(\beta_{pqr} \pm 3\sigma)$		
		1	**2**	**3**
0,1,1	$Cu(HL)^{2+}$	3.93±.09	5.63±.06	2.87±.04
0,1,2	$Cu(HL)_2{}^{2+}$	7.48±.09		5.29±.20
−1,1,1	CuL^+	0.90±.09		
−1,1,2	$Cu(HL)L^+$	5.43±.04	8.09±.03	1.97±.07
−2,1,2	CuL_2	−1.53±.04	−0.32±.05	−3.68±.12
−4,3,3	$Cu_3L_3OH^{2+}$	5.57±.12	9.78±.05	1.05±.03
−5,3,3	$Cu_3L_3O^+$ (or $Cu_3L_3(OH)_2{}^+$)	−0.97±.12	3.47±.06	
No. of points/titrations		360/12	450/12	306/8
χ^2		48.6	34.6	34.9
S		2.75	2.90	2.27

DISCUSSION

Slightly different sets of complexes were obtained for ligands **1**, **2** and **3**. Figure 2 shows that in most cases the difference is found in connection with the mononuclear complexes, which occur as relatively minor species in the most acidic conditions. Owing to the fairly large uncertainties in the measurements at low pH, firm conclusions cannot, however, be drawn from the interpretation of these sections of the data. The variations in the pH ranges available for the different ligands also affect the complexing models obtained. Thus with **3**, the experimental data was restricted to lower pH values than with **1** and **2**, and for this obvious reason the hydrolyzed trimer −5,3,3 was not detected with **3**.



Pyridine-2-carboxaldehyde oxime, (1)

1-(2-Pyridinyl)ethanone oxime, (2)

6-Methylpyridine-2-carboxaldehyde oxime, (3)

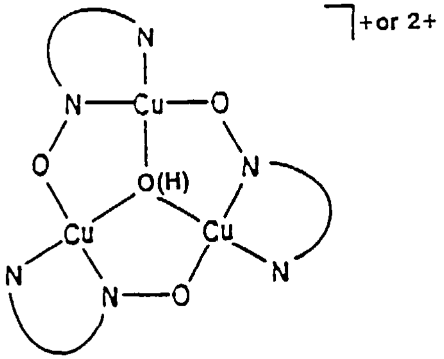
FIGURE 2 Concentration distribution diagram of the copper(II) species for C_L:C_M ratios 1 (C_L = C_M = 5 mM) and 2 (C_L = 10 mM, C_M = 5 mM). The computer program SPE[20] was used in the calculations.

Concerning the effect of the methyl substituents of the ligands on the complex stabilities, Table II shows that the values of logβ_{pqr} generally increase in the ligand order **3**<**1**<**2**. Interestingly, this sequence does not follow the basicities of the pyridine nitrogens, which increase in the order **1**<**2**<**3**. The apparent discrepancy can easily be explained by the steric influence of the 6-methyl group on complex formation, which causes the complexes formed with ligand **3** to be considerably less stable than could be predicted merely on the basis of its basicity. The decreasing effect of the 6-methyl group on the pyridine ring on the complex stability has been observed with other comparable instances, *e.g.* with complexes formed with methylated pyridine[16] and pyridine-2-carboxylate ligands.[17]

The trinuclear complex $-4,3,3$ was found for all the ligands. As can be seen from the species distribution diagrams in Figure 2, it may exist as a major species in all systems; under $C_L/C_M = 1$ conditions it even predominates in the pH range 4–6.

When the ligand to metal ratio is increased the proportion of $-4,3,3$ of the total metal concentration is rapidly reduced. This is especially true with ligands **1** and **2** and largely results from the increase in the relative amount of the major species $-1,1,2$ ($=$ Cu(HL)L$^+$). With **3**, formation of the bis complex is hindered by the presence of the 6-methyl group, and the corresponding $-4,3,3$ complex is preserved longer as the predominant species.

Our establishment of the formation of the aqueous $-4,3,3$ complex is in good agreement with results given earlier for **1** in the solid state.[18] Thus there can be little doubt about the actual structure of this species. Displacement of all three oxime protons and one aqua proton most probably yields a $Cu_3L_3OH^{2+}$ complex, which contains a central Cu_3OH core held by three peripheral oximato bridges, as shown schematically in the general formula below.



The O atom in the Cu_3OH unit is located above the Cu_3 plane and thus exhibits a roughly tetrahedral coordination sphere.[18,19]

With ligands **1** and **2**, existence of the trinuclear complex of composition $-5,3,3$ was confirmed. Figure 2 shows that in the $C_L/C_M = 1$ titrations it begins to appear at $pH \geq 5$. In neutral and alkaline solutions the metal is nearly completely bound to this species. The complex $-5,3,3$ can be considered to form from the parent trimer $Cu_3L_3OH^{2+}$ through deprotonation. The acidity of $Cu_3L_3OH^{2+}$ is about the same for both ligands, as shown by the pk_a values 6.54 (ligand **1**) and 6.31 (ligand **2**).

Although it can reasonably be assumed that the triangular central core Cu_3O is not ruptured upon deprotonation, the actual structure of $-5,3,3$ is uncertain. Whether this species is a dihydroxo complex, $Cu_3L_3(OH)_2{}^+$, or an oxo complex, $Cu_3L_3O^+$, cannot be decided on the basis of the potentiometric data. The latter alternative is nevertheless supported by an electrochemical study where a ready interconversion of Cu_3O and Cu_3OH was found in some mixed solvents.[3]

It may be noted that, in the solid complexes with Cu_3O cores, these cores are further bonded to another Cu_3O unit *via* a (weak) intertrimer Cu-O-Cu bond.[4] In solution this would correspond to a species of composition $-8,6,6$. No such hexanuclear complexes were found in this study.

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