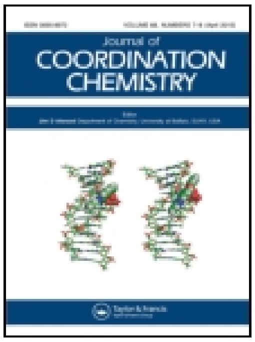

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Complexation of pyrazine-2-carboxamidoxime with Cu(II), Ni(II), Co(II), Zn(II), and Cd(II) ions in aqueous solution

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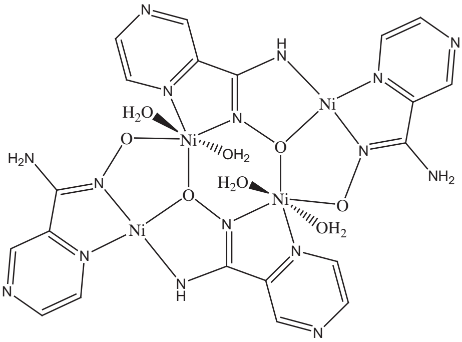

The protonation and complex formation equilibria of pyrazine-2-carboxamidoxime with Cu(II), Ni (II), Co(II), Zn(II), and Cd(II) ions in aqueous 0.1 mol L^{-1} NaCl solution were studied at 25 °C by potentiometric titration. The model for complexation and the stability constants of the different complexes were determined for each metal ion using SUPERQUAD.

Keywords: Stability constants; Pyrazine-2-carboxamidoxime; Metal complexes; Cu(II); Ni(II); Co (II); Zn(II); Cd(II)

1. Introduction

The equilibrium and structural studies of some pyridine-2-oximes [1–7] or aminoamidoximes of type $RR'N(CH_2)_nC(NH_2)NOH$ [8–13] with Cu(II), Ni(II), Co(II), Zn(II), and Cd(II) ions have been studied extensively and described previously. These bidentate oximes coordinate with divalent metal ions, mainly through their pyridine or amine and oxime nitrogens, forming five- or six-membered chelate rings. In the low pH range, oxime ligands coordinate as uncharged ligands, but their oxime (–NOH) groups deprotonate on increase in pH. The

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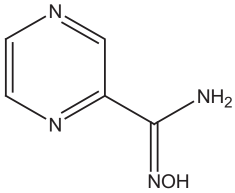
*Corresponding author. Email: markku.salonen@helsinki.fi deprotonated or hydrolyzed complexes can polymerize through the –NOH oxygen and the amidoxime complexes also through the amido group in the form $-NH^{-}-$. The formation of polynuclear complexes seems to increase when the stabilities of bis and tris complexes decrease.

Pyrazine-2-carboxamidoxime is analogous to pyridine-2-carboxamidoxime, which forms more stable complexes than do pyridine-2-carboxaldehyde oxime and its methyl-substituted derivatives [2–4]. Pyrazine-2-carboxamidoxime has been tested for medical applications due to its antibacterial activity. The emergence of drug-resistant pathogenic strains has resulted in a need for antibacterial and antituberculous drugs with improved properties. In studies on antibacterial and antituberculous agents active against multidrug-resistant strains, pyrazine-2-carboxamidoxime was active against both aerobic and anaerobic bacteria [14]. Pyrazine-2-carboxamidoxime is also a good ligand for the construction of polymeric networks with interesting magnetic properties [15]. To deepen our understanding of the protonation and complexation behavior of pyrazine-2-carboxamidoxime and to obtain information on the potential applications of this ligand, we extended our complexation studies on oxime ligands to include pyrazine-2-carboxamidoxime and report here its aqueous complexation with Cu(II), Ni(II), Co(II), Zn(II), and Cd(II) ions.



2. Experimental

2.1. *Preparation of pyrazine-2-carboxamidoxime, stock solutions of metal ions, and titration solutions*

Pyrazine-2-carboxamidoxime was synthesized by refluxing a suspension of 2.5 g hydroxylamine hydrochloride, 2 g Na_2CO_3, and 3.4 mL pyrazinecarbonitrile in 1 : 1 ethanol : water solution for two hours. The light yellow crystalline product was separated by filtering, washed with a small amount of water, and recrystallized from the water–ethanol mixture, as described previously [1, 14, 16, 17]. The melting point was 188 °C (lit. 185–187 °C) [14, 17]. Elemental analysis for pyrazine-2-carboxamidoxime ($C_5H_6N_4O$) calculated (%): C, 43.78; H, 4.378; N, 40.56. Found (%): C, 40.26; H, 4.487; N, 40.26. The purity of the preparation was confirmed by potentiometric titration.

Aqueous Cu(II), Ni(II), Co(II), Zn(II), and Cd(II) chloride solutions were prepared by dissolving p.a. grade $CuCl_2$, $NiCl_2$, $CoCl_2$, and $CdCl_2$ hydrates in distilled water and ZnO in aqueous hydrochloric acid. The metal contents of the stock solutions were standardized by EDTA titration. The Cu(II) concentration was also determined electrogravimetrically and the Ni(II) concentration mass analytically by precipitating with dimethylglyoxime. The acid contents of the metal solutions were determined by titration with 0.1 mol L^{-1} NaOH solution after liberation of H^+ by cation exchange. Aqueous 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl were prepared from Titrisol ampoules (Merck). Water used in the dilutions and titration solutions was purified with Milli-RO and Milli-Q water purification systems (Millipore).

2.2. *Potentiometric measurements*

The protonation and complex formation equilibria were studied in aqueous 0.1 mol L^{-1} NaCl at 25.0 °C through a series of potentiometric EMF titrations carried out with a Schott-Geräte GmbH titrator TPC2000 and utilizing titration software TR600 version 5.02 and with a pH-meter CG 841 (Schott). The cell arrangement for the measurement of the hydrogen ion concentration $[H^+]$ was as follows:

$$-\text{RE}\ |\text{equilibrium solution}|\ \text{GE}+ \tag{1}$$

where GE denotes a glass electrode (Schott N2680) and RE is Hg, Hg_2Cl_2 || 0.1 mol L^{-1} NaCl. Expression (2) is valid assuming the activity coefficients to be constant.

$$E = E_0 + 59.157\ \log[H^+] + j_H[H^+] + j_{OH}[OH^-] \tag{2}$$

The cell parameter E_0 and the liquid junction coefficient j_H, valid in acidic solutions, were determined for each titration by addition of a known amount of HCl to the background electrolyte. The value of the liquid junction coefficient j_{OH}, valid in basic solutions, was determined periodically. Only stable EMF readings were used in the calculations.

During measurements of the metal complex equilibria, aqueous 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl was added to the solution. The ratio of the total concentrations of metal (C_M) to ligand (C_L) was usually held constant. The initial concentrations were varied within the limits 0.4 mmol $L^{-1} \le C_M \le$ 9.6 mmol L^{-1} and 2.6 mmol $L^{-1} \le C_L \le$ 7.9 mmol L^{-1}, covering metal-to-ligand ratios from 2 : 1 to 1 : 10. In some runs, aqueous metal chloride was used as a titrant. Eight to eleven independent titrations were carried out for each system. The number of data points used in the calculations of the stability constants varied from 315 to 593 in the pH ranges 1.9–3.8 for Cu(II), 2.0–10.1 for Ni(II), 2.1–10.1 for Co (II), 2.1–8.0 for Zn(II), and 2.0–8.9 for Cd(II). In some titrations, the upper pH value was limited by the appearance of a precipitate. The reproducibility and reversibility of the equilibria were tested by performing forward (increasing pH) and backward (decreasing pH) titrations.

2.3. *Data treatment*

Protonation and deprotonation of the ligand were controlled by addition of HCl or NaOH. In evaluating the equilibrium constants, the following two-component equilibria were considered:

$$HL + H^+ \leftrightharpoons H_2L^+; \beta_{101} \tag{3}$$

$$HL \leftrightharpoons L^- + H^+; \beta_{-101} \tag{4}$$

$$pH^+ + qM^{2+} \leftrightharpoons (H^+)_p(M^{2+})_q; \beta_{pq_0} \tag{5}$$

The acid strength of the oxime group is very weak, and thus the value of the corresponding acidity constant in reaction (4) is not very accurate. It was reasonable, therefore, to choose the ligand as a component in the form of the uncharged oxime (HL) in the stability constants of a three-component (H^+, M^{2+}, and HL) system:

$$pH^+ + qM^{2+} + r(HL) \leftrightharpoons (H^+)_p(M^{2+})_q(HL)_r; \beta_{pqr} \tag{6}$$

The protonation constants of the ligand and the hydrolysis constants of the metal ions [18] were considered as known parameters in evaluation of the three-component system (6).

Mathematical analysis of the systems involves a search for complex models (*pqr*-triplets) and equilibrium constants for the complexes that best describe the experimental data. The calculations were carried out with the computer program SUPERQUAD [19]. The sample standard deviation s and the χ^2 statistics used as criteria in selection of the complex models were those given by the program. As a means to improve the confidence level, the error limits for the log β values determined in this study are reported as three times the standard deviation given by the program.

Curves of Z_H *versus* pH were drawn to visualize the experimental data sets. Z_H describes the average number of H^+ ions added or liberated per mole of ligand and is given by the relation,

$$Z_H = \left([H^+] - C_H - K_w[H^+]^{-1}\right)/C_L \tag{7}$$

where C_H denotes the total concentration of protons calculated over the zero level HL, H_2O, and M^{2+}.

3. Results and discussion

3.1. *Protolytic properties of pyrazine-2-carboxamidoxime*

When pH decreases, HL is protonated to H_2L^+ and deprotonated to L^- with increase in pH. The neutralization titrations show that the stepwise deprotonation of H_2L^+ to HL occurs in the pH range from 1 to 4 (Z_H from −1 to 0, see figure 1, the curve for ligand alone, solid line). The positive Z_H values obtained in the pH range higher than pH 10 show that in alkaline solution, one proton (from the oxime group, HL to L^-) can leave the ligand (see figure 1, the curve for ligand alone, solid line). The equilibrium constants relating to the protolytic reactions of the ligand were evaluated from the experimental data of 211 titration points from four titrations ($\chi^2 = 5.83$, $s = 2.63$). The equilibrium constants for reactions (3) and (4) obtained in the final refinements are listed in table 1.

Under our measurement conditions, pyrazine-2-carboxamidoxime (HL) can accept only one proton. Possible sites to protonate include the nitrogen in a pyrazine ring or in an amide ($-NH_2$) group. Pyrazine (log $\beta_{101} = 0.65$ [20]) is a much weaker base than pyridine (log $\beta_{101} = 5.02$–5.48 [21]). The oxime group weakens the basicity of the pyridine nitrogen in pyridine-2-carboxamidoxime (log $\beta_{101} = 3.80$), but in pyridine-2-acetamidoxime (log $\beta_{101} = 5.02$), the effect is smaller [1]. From this point of view, it is not likely that the protonation is connected to the pyrazine ring nitrogen. The amide ($-NH_2$) group of pyridine-2-acetamidoxime is protonated with a stepwise protonation constant log $K_{201} = 2.27$ [1], which is very similar to the protonation constant of pyrazine-2-carboxamidoxime

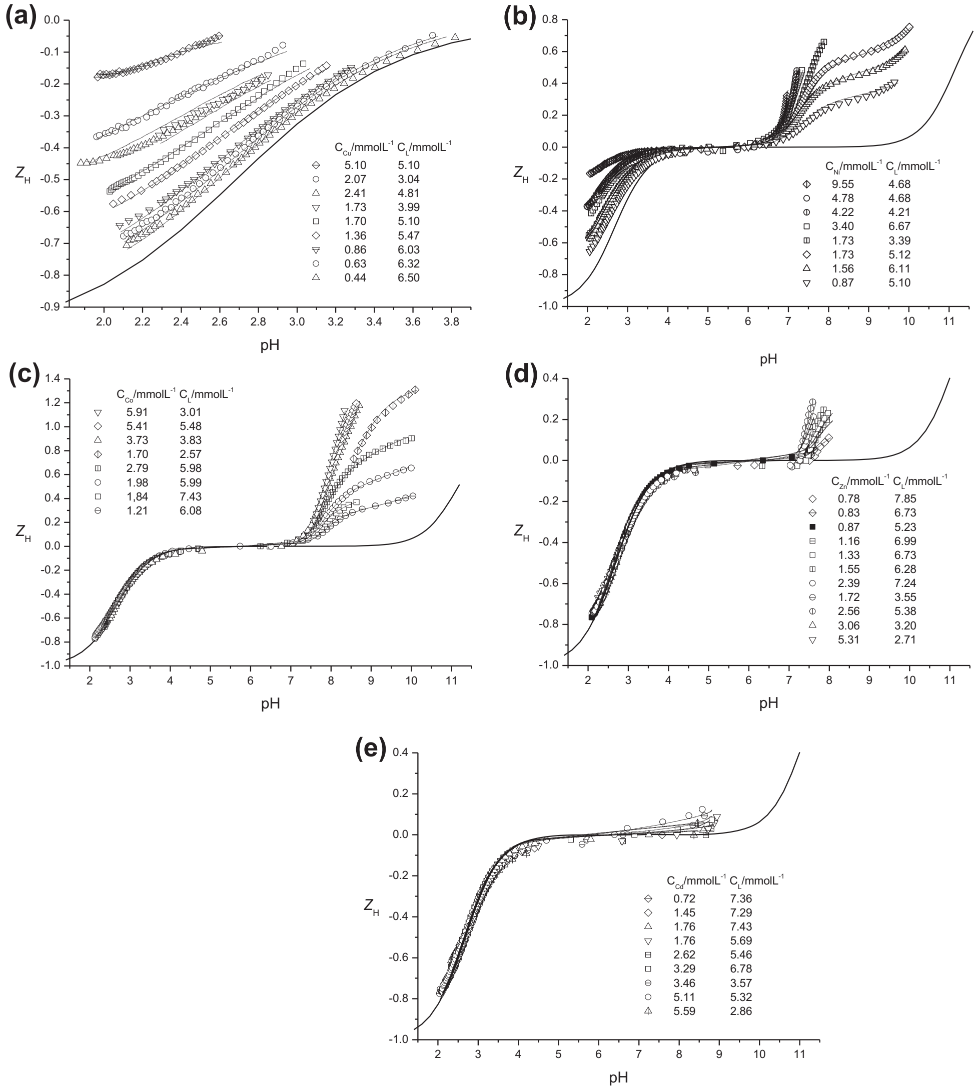


Figure 1. Z_H *vs.* pH for complexation of (a) Cu(II), (b) Ni(II), (c) Co(II), (d) Zn(II), and (e) Cd(II) ions with pyrazine-2-carboxamidoxime (symbols = measured Z_H, dotted line = calculated Z_H for complexation, solid line = Z_H for pyrazine-2-carboxamidoxime).

(log β_{101} = 2.68). So it is possible that under our measurement conditions, the amide group of pyrazine-2-carboxamidoxime protonates instead of the pyrazine ring. In alkaline solution, the oxime (–NOH) group of the ligand deprotonates according to reaction (4). The pK_a value 11.17 shows that the acidity of the oxime in pyrazine-2-carboxamidoxime (HL) is somewhat higher than in several amino and pyridine amidoximes (11.5–12.5) [1, 8–12].

3.2. *Complexation with Cu(II), Ni(II), Co(II), Zn(II), and Cd(II)*

Analysis of the data was initiated by drawing curves of Z_H *versus* pH (figure 1). For all metal ions, the complexation begins at very acidic pH, although the complexation is clearly

Table 1. Protonation and complexation of pyrazine-2-carboxamidoxime with Cu(II), Ni (II), Co(II), Zn(II), and Cd(II) ions in 0.1 mol L^{-1} NaCl aqueous solution at 25 °C[a].

	pqr	log ($\beta_{pqr} \pm 3\sigma$)	Proposed formula
H^+			
	101	2.68 ± 0.01	H_2L^+
	−101	−11.17 ± 0.02	L^-
χ^2/s	5.83/2.63		
Points/titrations	211/4		
Cu(II)			
	011	4.16 ± 0.05	$Cu(HL)^{2+}$
	012	6.63 ± 0.05	$Cu(HL)_2^{2+}$
	−112	2.52 ± 0.20	$Cu(HL)L^+$
	−110	−8.3	$CuOH^+$
χ^2/s	34.98/1.53		
Points/titrations	351/10		
Ni(II)			
	011	3.36 ± 0.07	$Ni(HL)^{2+}$
	012	5.97 ± 0.13	$Ni(HL)_2^{2+}$
	−112	−1.22 ± 0.20	$Ni(HL)L^+$
	013	8.37 ± 0.23	$Ni(HL)_3^{2+}$
	−113	1.27 ± 0.45	$Ni(HL)_2L^+$
	−213	−6.02 ± 0.07	$Ni(HL)L_2$
	−313	−16.12 ± 0.06	NiL_3^-
	−323	−9.06 ± 0.06	$Ni_2L_3^+$
	−644	−21.70 ± 0.19	$Ni_4L_2(L\text{-}H)_2^{2+}$
	−110	−10.06	$NiOH^+$
χ^2/s	43.26/1.61		
Points/titrations	593/9		
Co(II)			
	011	1.81 ± 0.08	$Co(HL)^{2+}$
	−112	−3.59 ± 0.23	$Co(HL)L^+$
	−322	−16.57 ± 0.09	$Co_2L_2OH^+$
	−422	−25.67 ± 0.16	$Co_2L_2(OH)_2$
	−323	−13.53 ± 0.07	$Co_2L_3^+$
	−423	−22.87 ± 0.23	Co_2L_3OH
	−110	−9.85	$CoOH^+$
χ^2/s	33.79/2.11		
Points/titrations	349/8		
Zn(II)			
	011	1.39 ± 0.24	$Zn(HL)^{2+}$
	−322	−15.72 ± 0.07	$Zn_2L_2OH^+$
	−110	−9.15	$ZnOH^+$
χ^2/s	11.08/2.87		
Points/titrations	384/11		
Cd(II)			
	011	1.27 ± 0.18	$Cd(HL)^{2+}$
	−111	−7.25 ± 0.14	CdL^+
	−110	−10.31	$CdOH^+$
χ^2/s	19.60/2.84		
Points/titrations	315/9		

[a]The binary hydrolysis constants were extrapolated to ionic strength 0.1 mol L^{-1} by the data and equations in Ref. [18].

stronger for Cu(II) and Ni(II) than for Co(II), Zn(II), and Cd(II) ions in acidic solution (the curves for complexation differ from those for protonation in figure 1). The solutions of Cu (II) were light green at the beginning but darkened or became yellow during titration. Precipitation occurred at pH values over 3.8. Thus, the pH range available to SUPERQUAD calculation was very narrow. The solutions of Ni(II) were colorless or green at the beginning but became yellow at pH 6–7 and orange and finally dark red further during titrations. In measurements with Ni(II), the titrations could be also performed in basic range up to pH 10.1 without precipitation. The Co(II) solutions were nearly colorless or slightly yellowish red-brown at the beginning of the titrations and the dark reddish brown color increased in the basic pH range. In measurements with Co(II), the titrations could be performed in basic range up to pH 11.8 without precipitation. In the case of Zn(II) and Cd(II) ions, the solutions were colorless at acidic pH and became slightly yellow at basic pH. The titrations could be performed without precipitation up to pH 8 for Zn(II) and up to pH 9 for Cd(II).

The complexation of pyrazine-2-carboxamidoxime with Cu(II) could be explained with a simple model containing $Cu(HL)^{2+}$ as the main species and a bis complex $Cu(HL)_2^{2+}$. However, the fit was significantly improved by addition of $Cu(HL)L^+$ (the improvement in χ^2/s values was from 52.72/1.69 to 34.98/1.53). No other species could be added to the model. The value of the acidity constant for $Cu(HL)_2{}^{2+}$ ($pK_a = 4.11$) is reasonable compared, e.g., with the value for the corresponding pyridine-2-carboxamidoxime complex ($pK_a = 4.61$) [1], taking into account the pK_a values of the oxime groups in pyrazine-2-carboxamidoxime (11.17) and pyridine-2-carboxamidoxime (11.7) [1].

For the Ni(II) ion, the formation of $Ni(HL)^{2+}$, $Ni(HL)_2^{2+}$, and $Ni(HL)_3^{2+}$ was observed in acidic pH range. The deprotonation of these species at pH > 6 can be seen in the Z_H curves in which $C_L > C_M$. In addition to these species, some polynuclear complexes were included in the SUPERQUAD calculations. The best fit to the experimental data was obtained when $Ni_2L_3^+$ and $Ni_4L_2(L–H)_2^{2+}$ were added to the mononuclear species $Ni(HL)^{2+}$, $Ni(HL)_2^{2+}$, Ni (HL)L^+, $Ni(HL)_3^{2+}$, $Ni(HL)_2L^+$, $Ni(HL)L_2$, and NiL_3^- ($\chi^2 = 43.26$, $s = 1.61$). The species $Ni_2L_3^+$ was also observed for 1-(2-pyridinyl)ethanone oxime and 6-methylpyridine-2-aldoxime [4]. The tetramer $Ni_4L_2(L–H)_2^{2+}$ was also recently found for pyrazine-2-carboxamidoxime in X-ray studies [15].

For the Co(II) ion, the formation of $Co(HL)^{2+}$ was found in acidic pH range, while in the basic pH range, $Co(HL)L^+$ and some polynuclear complexes were included in the calculations. The best fit to the experimental data was obtained when $Co_2L_3^+$, $Co_2L_2OH^+$, Co_2L_3OH, and $Co_2L_2(OH)_2$ (which can be seen in the Z_H curves) were added to the complexation model ($\chi^2 = 33.79$, $s = 2.11$). The polynuclear $Co_2L_3^+$, $Co_2L_2OH^+$, and Co_2L_3OH species were also found for 6-methylpyridine-2-aldoxime [5].

The Z_H curves of the Zn(II) and Cd(II) solutions dispersed only weakly at pH 2–7 showing only weak complex formation and exceeded the zero level at pH values over 7 demonstrating that some deprotonated complexes were formed. The best fit with the experimental data was obtained by focusing on only the two Zn(II) complexes $Zn(HL)^{2+}$ and $Zn_2L_2OH^+$ ($\chi^2 = 11.08$, $s = 2.87$, 384 points from 11 titrations) and the two Cd(II) complexes Cd (HL)$^{2+}$ and CdL^+ ($\chi^2 = 19.60$, $s = 2.84$). The same kind of complexation models with the Zn(II) and Cd(II) ions was also found previously for pyridine-2-acetamidoxime [7].

Table 1 shows the proposed formulas of the species, with the corresponding formation constants from equation (6) found in the equilibrium analysis of the different H^+–M^{2+}–HL systems. The percentage distribution of the metal ions among the different complex species is illustrated as a function of pH in the millimolar concentration range ($C_M = 1$ mmol L^{-1}, $C_L = 3$ mmol L^{-1}) in figure 2.

3.3. *Discussion*

The five divalent metal ions formed less stable mononuclear complexes with pyrazine-2-carboxamidoxime than with many other amidoximes, including pyridine-2-acetamidoxime [1, 5] and 3-(methylamino)propanamidoxime, which form six-membered chelate rings [11, 12]. This is despite the fact that pyrazine-2-carboxamidoxime forms five-membered chelate rings that are generally more stable than six-membered rings. The decisive factor is clearly the weaker basicity of the pyrazine nitrogen atom.

n addition to the percentage distribution of the different complex species *versus* pH (figure 2), the complexation of Ni(II) can also be illustrated by the following scheme with log values.

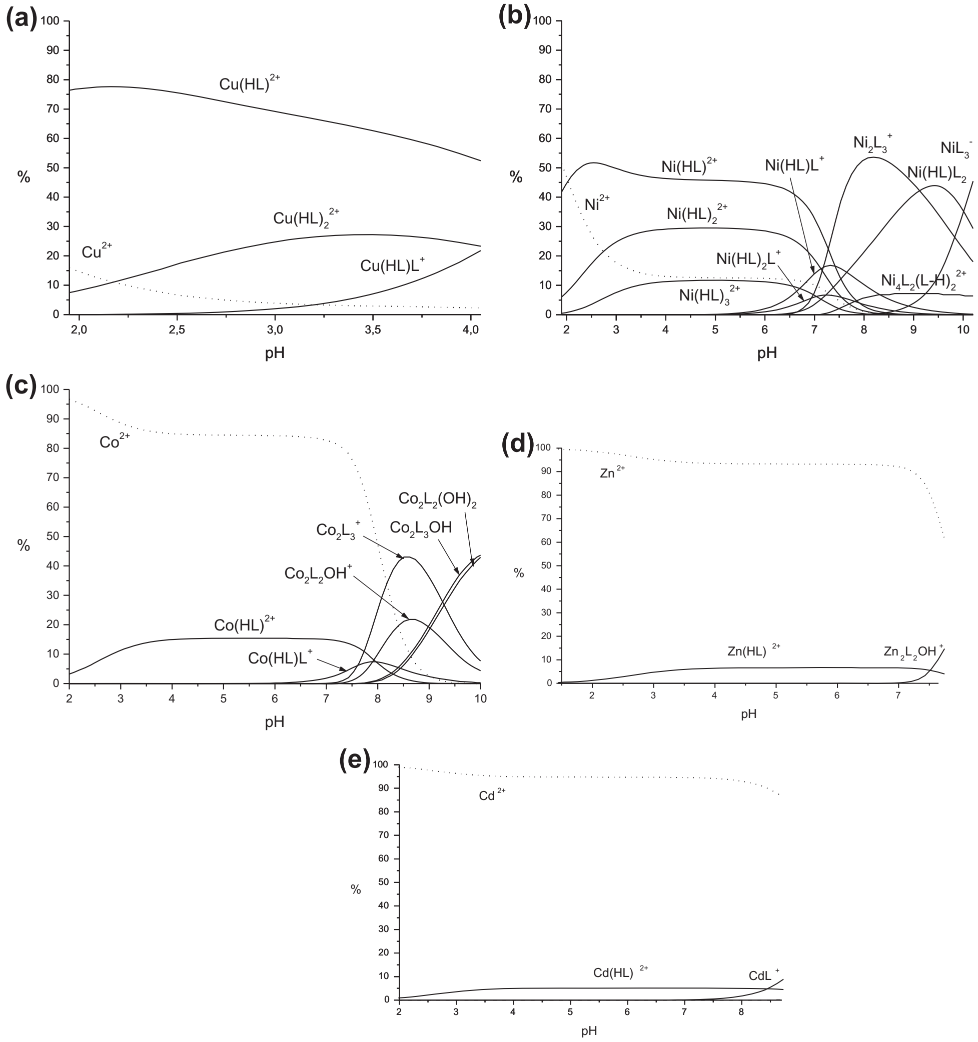


Figure 2. Percentage distribution of the different (a) Cu(II), (b) Ni(II), (c) Co(II), (d) Zn(II), and (e) Cd(II) complexes of pyrazine-2-carboxamidoxime as a function of pH (C_M = 1 mmol L^{-1}, C_L = 3 mmol L^{-1}).

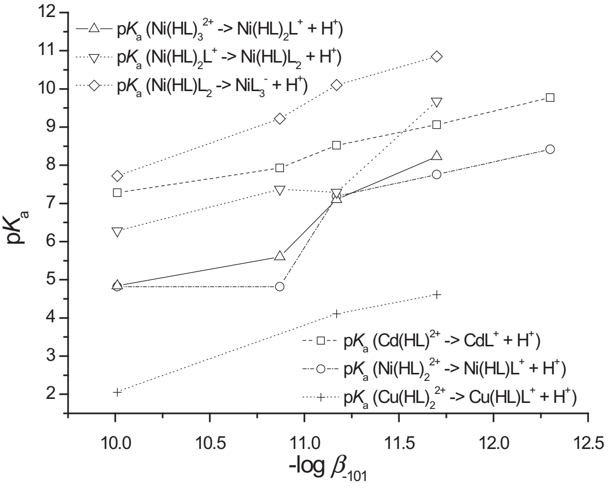
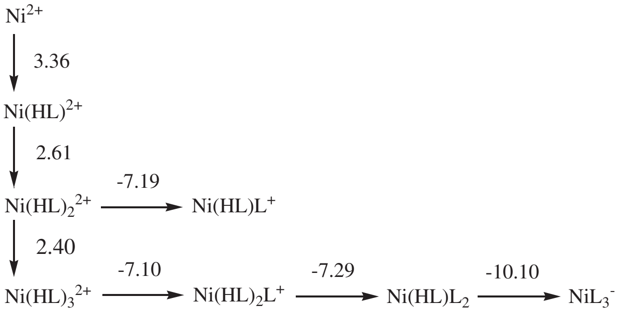


Figure 3. Relationship between $-\log \beta_{-101}$ and pK_a values for different metal complexes and reactions. Compounds from left to right: 1-(2-pyridinyl)ethanone oxime, 6-methylpyridine-2-carboxaldehydeoxime, pyrazine-2-carboxamidoxime, pyridine-2-carboxamidoxime, pyridine-2-acetamidoxime [1, 2, 4–7].



The scheme is very similar to those reported for pyridine-2-carboxamidoxime [1], pyridine-2-aldoxime [3], and 1-(2-pyridinyl)ethanone oxime [4]. In all these systems, the deprotonated mono complex NiL^+ is missing, but unlike the other systems, the twice deprotonated bis complex NiL_2 is also missing in this system. The acidity constants of the individual complexes were clearly dependent on the acidity of the oxime –NOH groups of the free ligand (see figure 3, which shows the relationship between the $-\log \beta_{-101}$ and pK_a values for different oxime ligands, metal ions, and reactions).

Based on several studies of similar compounds [1, 9, 10, 22], the deprotonated bis complexes $Ni(HL)L^+$, $Cu(HL)L^+$, and $Co(HL)L^+$ have an intramolecular hydrogen bridge (=N–O–H···$^-$O–N=) between the oxygens of adjacent oxime groups. That weakens their acidities. This and the stronger ligand fields of the deprotonated tris complexes are the reasons for the disappearance of the $Ni(HL)L^+$ complex at pH 9–10 (see figure 2) without observation of NiL_2.

The solutions are colorless or green in the pH range 2–6 showing that the present species Ni^{2+}, $Ni(HL)^{2+}$, $Ni(HL)_2^{2+}$, $Ni(HL)_3^{2+}$, and $Ni(HL)L^+$ are octahedral with high spin electron structures ($t_{2g}^6 e_g^2$). In the pH range 6–7, in which $Ni(HL)_2L^+$ and $Ni(HL)L^+$ appear, the

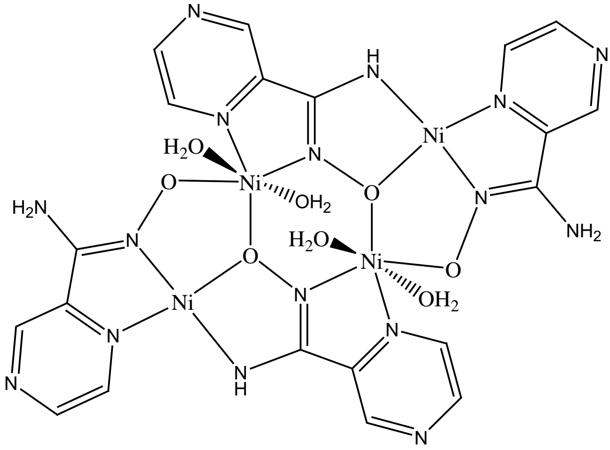


Figure 4. A schematic presentation of the tetranuclear complex ion $Ni_4L_2(L–H)_2^{2+}$ projected on a plane.

solutions are yellow and become orange and finally red with increase in pH, when $Ni_2L_3^+$, $Ni(HL)L_2$, $Ni_4L_2(L–H)_2^{2+}$, and NiL_3^- are formed. The reddish color in the solutions usually refers to square-planar low spin complexes.

The tetranuclear Ni(II) complex $Ni_4L_2(L–H)_2^{2+}$ is probably formed through bonding and deprotonation of two mono complexes via two oximato (–NO$^-$–) bridges to $Ni_2L_2^{2+}$, which is further polymerized via amido –NH$^-$– and oximato –NO$^-$– bridges. Structural studies [15] showed that the two last mentioned Ni(II) ions are in the solid red-brown $Ni_4L_2(L–H)_2^{2+}$ surrounded by one oxygen and three nitrogens with square planar but the two others by four oxygen and two nitrogen atoms with octahedral coordination (see figure 4).

The small difference between the stepwise stability constants of the pyrazine-2-carboxamidoxime complexes $Ni(HL)_2^{2+}$ (log $K_2 = 2.61$) and $Ni(HL)_3^{2+}$ (log $K_3 = 2.40$) and especially the strong acidity of $Ni(HL)_3^{2+}$ (p$K_{a1} = 7.10$ and p$K_{a2} = 7.29$) in relation to the acidity of the oxime –NOH groups of the free pyrazine-2-carboxamidoxime (see figure 3) showed strengthening of the ligand field in the stepwise formation of the tris complex $Ni(HL)_3^{2+}$ and in its deprotonation to $Ni(HL)L_2$. The deprotonation of the oxime group shortens the bond between the metal and the oxime nitrogens and strengthens the ligand field around the central metal. Spin pairing in the Ni(II) ion requires a remarkable distortion of its octahedral coordination or opening of one or two chelate rings. In the five-coordinate square-pyramidal or trigonal bipyramidal complexes, the two least stable d orbitals are not degenerate [23]. This leads to the conclusion that spin pairing and distorted octahedral structure or five-coordination may also partly explain the color of the solution in the case of $Ni_2L_3^+$ and $Ni(HL)L_2$, which are present at pH values in which a red color occurs.

However, the red-orange color of the solution does not always necessarily indicate existence of square-planar or diamagnetic low spin Ni(II) complexes. Previous studies have also associated an orange color with paramagnetic (high spin) complexes. For example, in the presence of eightfold pyridine-2-aldoxime excess, the nickel(II) ion is at pH ≈ 8 and $C_M \approx 10^{-2}$ M almost totally as $Ni(Hpa)(pa)_2$ and $Ni(pa)_3^-$ [3], but although both of the tris complexes are equally paramagnetic to the aqua ion Ni^{2+} [24, 25], the solutions are orange [26]. Thus, the octahedral diamagnetic pyrazine-2-carboxamidoxime complexes of Ni(II) can also be responsible for the orange-red color of solutions.

The connection often found between the ternary hydrolytic metal complexes and binary hydroxo species [27–32] would suggest that the binary hydrolytic core $Ni_4(OH)_4^{4+}$ would give rise to the ternary hydroxo complex $Ni_4(OH)_4(HL)_2L_2^{2+}$. However, the tetramer is not deprotonated at pH 9-10 (figure 2). Thus, the binary structure $Ni_4L_2(L–H)_2^{2+}$ is also much more probable for the tetramer in aqueous solution in addition to the solid state. Tetramers with similar coordination have also been found for complexation of Cu(II) and Ni(II) with 2-(dimethylamino)-acetamidoxime and 2-(diethylamino)acetamidoxime [8–10], and for Ni (II) [15], Zn(II) and Cd(II) ions with pyridine-2-carboxamidoxime [7].

$Ni_2L_3^+$ and $Co_2L_3^+$ are probably formed through deprotonation and combination of a mono and a bis complex via three oximato bridges. In $Co_2L_3^+$, one of the Co(II) ions surrounded by four nitrogens (two oxime and two pyrazine nitrogens) is probably low spin but the other surrounded by two nitrogens (oxime and pyrazine nitrogens) is of high spin. The octahedral low spin part ($t_{2g}^6e_g$) and one of the oximato bridges is Jahn–Teller distorted. The deprotonation of $Co_2L_3^+$ to Co_2L_3OH in the pH range 8–9 requires formation of a hydroxo bridge between the cobalt(II) ions and breaking of an oximato bridge, if the coordination spheres of Co_2L_3OH are still octahedral. The Jahn–Teller distorted oximato bridge of $Co_2L_3^+$ is easily broken and after bending of the remaining $(CoNO)_2$ ring, the hydroxo –OH^-– bridge is formed on the opposite side of the opened oximato (–NO^-) group. In $Ni_2L_3^+$, none of the three oximato bridges is Jahn–Teller distorted. During increase in pH, $Ni_2L_3^+$ is displaced by the tris complexes without deprotonation to Ni_2L_3OH. Similarly, 6-methylpyridine-2-aldoxime (Hmp) forms $Co_2(mp)_3^+$ and $Ni_2(mp)_3^+$ in aqueous solution, but only $Co_2(mp)_3^+$ is deprotonated (with $pK_a = 7.7$) to $Co_2(mp)_3OH$ [5]. $Ni_2(mp)_3^+$ is displaced by $Ni_3(mp)_3(OH)_2^+$ in the pH range 8–9, but $Ni_2(mp)_3OH$ is unknown [4].

The ternary binuclear hydroxo complexes $Co_2L_2OH^+$ and $Zn_2L_2OH^+$ are probably formed through deprotonation and dimerization of two mono complexes $M(HL)^{2+}$ via two oximato bridges to $M_2L_2^{2+}$, which is immediately deprotonated further to $M_2L_2OH^+$ by forming a hydroxo –OH^-– bridge in addition to the six-membered ring consisting of two M–N–O units. The alternative binuclear structure $M_2(L–H)L^+$ or $M(L–H)ML^+$, in which the metal ions are combined by an oxime and an amido nitrogen of the ligand (L–H), can be excluded, because the pH range 7–8 at which the dimers occur is too low for deprotonation of the oxime group of pyrazine-2-carboxamidoxime without coordination. During increase in pH, the complex is deprotonated further to $Co_2L_2(OH)_2$. The amount of $Zn_2L_2OH^+$ is small before hydroxide precipitation occurs and prevents observation of further deprotonation.

According to the spectrochemical series of ligands [23], the hydrolysis of aqua ligands weakens the ligand field around the metal ion. So the hydrolysis of the aqua ions weakens the ligand fields in the order Co^{2+} ($\log \beta_{-110} = -9.85$) > Ni^{2+} (-10.06) < Zn^{2+} (-9.15). For the same reason, $Co_2L_2OH^+$ ($\log \beta_{-322} = -16.57$) is less stable than $Zn_2L_2OH^+$ (-15.72), although $Co(HL)^{2+}$ is more stable than $Zn(HL)^{2+}$. This also holds for the corresponding 6-methylpyridine-2-aldoxime (Hmp) complexes $Co_2(mp)_2OH^+$ ($\log \beta_{-322} = -14.81$) and $Zn_2(mp)_2OH^+$ (-14.55) [5, 6]. In this respect, it is surprising that the pyrazine-2-carboxamidoxime complex $Co_2L_2^{2+}$ does not polymerize further via amido –NH^-– bridges to a tetramer. No polynuclear cobalt(II) complexes with amido –NH^-– bridges have been reported.

The larger size of the Cd(II) weakens its electrostatic forces in the Cd–O bonds, and in this way, the polymerization of the deprotonated mono complex CdL^+ via oximato –NO^-– bridges. $Cd(OH)_2$ is precipitated before any polymerization of the pyrazine-2-carboxamidoxime complex CdL^+. The relationship between the acidities of $Cd(HL)^{2+}$ ($pK_a = 8.52$) and the free pyrazine-2-carboxamidoxime correlate well with the other mono complexes of the Cd(II) ion, which are acids 2–3 log units stronger than the free ligands (figure 3).

Figure 3 shows the relationship between the –log β_{-101} and pK_a values for different metal ions and reactions for 1-(2-pyridinyl)ethanone oxime, 6-methylpyridine-2-carboxaldehydeoxime, pyrazine-2-carboxamidoxime, pyridine-2-carboxamidoxime, and pyridine-2-acetamidoxime. In each case, the pK_a value for a certain reaction increases with increasing −log β_{-101} value [1, 2, 4–7].

4. Conclusion

By comparing the results with those obtained previously, the stability of the mono complexes $M(HL)^{2+}$ (and bis complexes $M(HL)_2^{2+}$) increases, with few exceptions, in the order 6-methylpyridine-2-aldoxime < pyrazine-2-carboxamidoxime < pyridine-2-acetamidoxime < pyridine-2-aldoxime < 1-(2-pyridinyl)ethanone oxime < pyridine-2-carboxamidoxime and Cd < Zn < Co < Ni < Cu [1–7] according to the Irving–Williams order for divalent transition metal ions [33]. The 4-nitrogen of the pyrazine ring markedly weakens the ability of the 1-nitrogen–metal bonds of the pyrazine-2-carboxamidoxime complexes in comparison with the corresponding pyridine-2-carboxamidoxime complexes.

During increase in pH, the complexes are deprotonated and especially the deprotonated mono complexes are polymerized via oximato bridges. The amidoximes can also polymerize via amido bridges. The formation of polynuclear complexes clearly originates from the weak stability of the mononuclear bis (and tris) complexes. The polymerization of the complexes provides several alternative ways for metal ions to complete their octahedral coordination spheres. The weak acidity of the oxime NOH group of pyrazine-2-carboxamidoxime prevents the formation of polynuclear complexes in the acidic pH range.

Disclosure statement

No potential conflict of interest was reported by the authors.

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