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## Formation of cobalt(II) complexes with five pyridine oximes in aqueous solution

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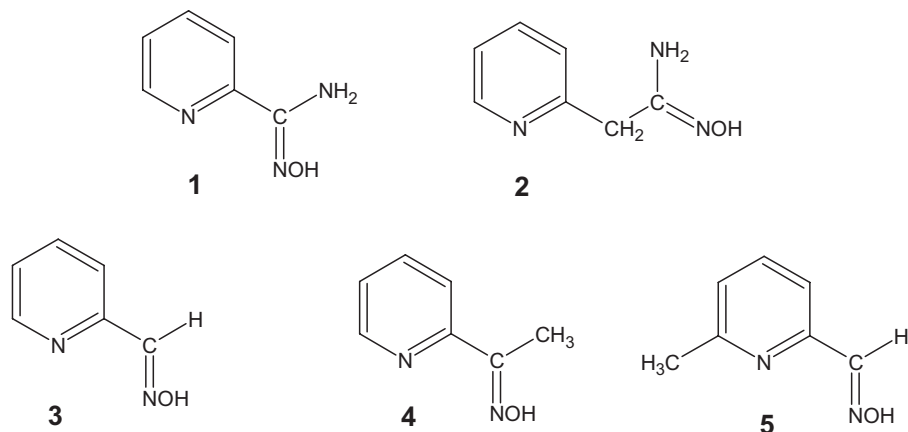
Complex formation equilibria of cobalt(II) with pyridine-2-carboxamidoxime (**1**), pyridine-2-acetamidoxime (**2**), pyridine-2-aldoxime (**3**), 1-(2-pyridinyl)ethanone oxime (**4**) and 6-methylpyridine-2-aldoxime (**5**) were studied in 0.1 M NaCl solution at 25°C by potentiometric titrations with 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 ligands **1–4** Co(II) forms mono, bis and (except for **2**) tris complexes of the type  $\text{Co}(\text{HL})_r^{2+}$  and deprotonated/hydrolyzed products of the bis and tris complexes,  $\text{Co}(\text{HL})\text{L}^+$  and  $\text{Co}(\text{HL})_2\text{L}^+$ . The deprotonated complexes have a low spin structure ( $t_{2g}^6 e_g$ ) and are readily oxidized after the easy loss of the sole  $e_g$  electron. Their formation with increasing pH involves slow attainment of equilibrium in the pH range 3–5. Only with ligand **3** could studies be continued to pH 8–10 by using very low cobalt(II) ion concentrations. There,  $\text{CoL}_2$  is formed quantitatively, while complexes  $\text{Co}(\text{HL})\text{L}_2$  and  $\text{CoL}_3^-$  could not be observed. Ligand **1** also forms the complex  $\text{Co}_2(\text{HL})_2\text{H}_2\text{L}^{5+}$  and ligand **2** the complex  $\text{Co}(\text{H}_2\text{L})^{3+}$  with the positively charged ligand ( $\text{H}_2\text{L}^+$ ). Ligand **5** forms the complexes  $\text{Co}(\text{HL})^{2+}$ ,  $\text{CoL}_2$ ,  $\text{Co}_2\text{L}_2\text{OH}^+$ ,  $\text{Co}_2\text{L}_3^+$  and  $\text{Co}_2\text{L}_3\text{OH}$  mainly in the pH range 6–10. The stabilities of these complexes and also their oxidation reactions are reduced by the steric requirements of the 6-methyl groups of the ligand.

**Keywords:** Cobalt(II) complexes; Pyridine oximes; Equilibria; Stability constants

### 1. Introduction

In earlier papers we described the complexation of the pyridine-2-oximes **1–5** in aqueous solution [1–6]. Mononuclear pyridine oxime complexes and their deprotonated/hydrolyzed products  $\text{H}_p\text{M}(\text{HL})_r^{2+}$  ( $p = 0, -1, -2, -3$ ;  $r = 1, 2, 3$ ) were observed with all ligands. Di- and trinuclear complexes with ligands **3–5**, for example  $\text{M}_2\text{L}_2^{2+}$ ,  $\text{M}_2\text{L}_2\text{OH}^+$  and  $\text{M}_2\text{L}_2(\text{OH})_2$  with  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ ,  $\text{Ni}_2\text{L}_3^+$  (with **4** and **5**),  $\text{Ni}_3\text{L}_3(\text{OH})_2^+$  (with **5**)  $\text{Cu}_3\text{L}_3\text{OH}^{2+}$  and  $\text{Cu}_3\text{L}_3\text{O}^+$  also have been observed. The stability constants of mononuclear complexes of type  $\text{M}(\text{HL})_r^{2+}$  with  $r = 1, 2$  or 3 generally increase in the ligand order  $5 < 2 < 3 < 4 < 1$  [1–6]. In this work we extend the studies with these five pyridine oximes to complexation of the divalent cobalt ion.

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## 2. Experimental

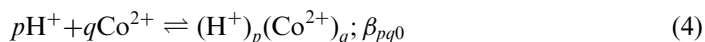
### 2.1. Reagents and solutions

Pyridine-2-aldoxime, **3**, (99+ % Aldrich, gold label) was used without further purification. Pyridine-2-carboxamidoxime, **1**, pyridine-2-acetamidoxime, **2**, 1-(2-pyridinyl)ethanone oxime, **4**, and 6-methylpyridine-2-aldoxime, **5**, were prepared according to methods described earlier [1,2]. The stock solution of CoCl<sub>2</sub> was standardized against EDTA using murexide as indicator.

### 2.2. Methods

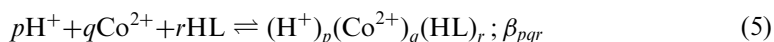
The investigation was carried out as a series of potentiometric titrations in aqueous 0.1 M NaCl solutions at 25.0°C. Because of the poor solubility of some of the most interesting complexes in perchlorate solutions, NaCl was chosen instead of the more common NaClO<sub>4</sub>. The electrode system used in the measurements and its calibration to hydrogen 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 by very slow attainment of equilibrium.

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



The acid strengths of the oxime groups are very weak, and thus the values of the corresponding  $pK_a$  values in reaction (3) are not very accurate. It was reasonable, therefore, to choose the ligand as a component in the form of the uncharged oxime

(HL) in evaluating the stability constants of a three-component ( $H^+$ ,  $Co^{2+}$  and HL) system (5):



In the evaluation of the three-component experimental data, the binary complex models were considered as known. The protonation constants of the ligands are given together with the results for that ligand. For the binary hydrolytic equilibrium of cobalt(II), reaction (4), we used the values  $\log \beta_{-110} = -9.85$  and  $\log \beta_{-210} = -19.02$  [8]. No attention was paid to the possible formation of chloro complexes.

The mathematical analysis of data was performed with the least-squares computer program SUPERQUAD [9]. The  $pqr$  triplets and corresponding equilibrium constants that best fit the experimental data were determined by minimizing the error sum  $U = \sum w_i (E_i^{obs} - E_i^{calc})^2$ . The weighting factor  $w_i$  was determined by the equation  $w_i = 1/(\sigma_E^2 + \delta E_i / \delta V_i) \sigma_V^2$ , where  $\sigma_E$  ( $= 0.1$  mV) and  $\sigma_V$  ( $= 0.02$  cm<sup>3</sup>) 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 complex model that best describes the experimental data were  $\chi^2$  statistics and the sample standard deviation,  $s$  [10].

### 3. Results and discussion

In the systems for ligands **1–4**, the stable pH range was narrow, in most cases 2–5. Only solutions of ligand **5** and some solutions of **3** with very dilute cobalt(II) concentrations could be titrated to pH range 8–10. The likely reason for the narrow pH range is the formation of octahedral low spin cobalt(II) complexes and their oxidation to cobalt(III) complexes. Almost all the cobalt(III) complexes are octahedral and low spin state ( $t_{2g}^6$ ) [11]. Because both  $e_g$  orbitals are empty and all  $t_{2g}$  orbitals are occupied [12], the cobalt(III) complexes are chemically inert. Their ligand exchange reactions are slow and attainment of equilibrium usually takes many months [11].

A possible oxidant is oxygen from the air dissolved in the reaction mixture, even though in all titrations nitrogen gas was passed through the solutions during the whole titration. During and after the addition of NaOH, high local concentrations of  $OH^-$  ion and low spin cobalt(II) complexes (e.g.,  $Co(HL)L^+$  and possibly also complexes like  $CoL_2$ ) may be momentarily formed before mixing of the solution is complete. The final color of the solutions formed during titration was preserved during back titration with HCl solution, indicating that the oxidation reaction are irreversible. The low  $\chi^2$  and  $s$  values indicate, however, that amounts of the possible cobalt(III) complexes were still small in the pH ranges tested.

The low spin cobalt(II) complexes are Jahn–Teller distorted due to the uneven electron occupation in the  $e_g$  orbitals. Few six-coordinate low spin cobalt(II) complexes have actually been reported and none has been structurally characterized [11]. In this work, all evaporated solutions (room temperature) left only a powder (usually very hygroscopic) and NaCl crystals. No complexes could be structurally characterized by X-ray diffraction.

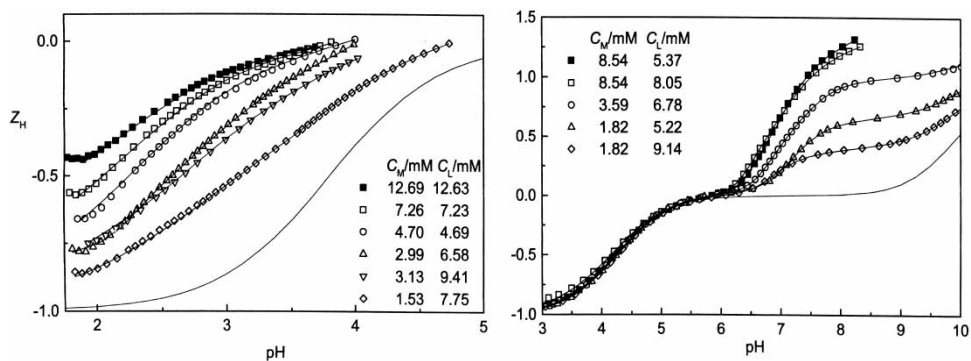


Figure 1. A portion of the experimental data plotted as curves  $Z_H$  vs pH for ligands **1** (left) and **5** (right). The full lines have been calculated using sets of proposed stability constants as given in table 1. The lowest line refers to the ligand alone.

We calculated experimental results in terms of sets of  $Z_H$  versus pH.  $Z_H$  is defined as the average number of OH<sup>-</sup> 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 hydrogen ions calculated over the zero level HL, H<sub>2</sub>O and Co<sup>2+</sup>. The plots for ligands **1**–**4** are closely similar and do not exceed the zero level, unlike the plot for **5**. Figure 1 shows plots for **1** and **5**.

### 3.1. The Co<sup>2+</sup>–ligand 1 system

A series of solutions with different concentrations of cobalt(II) ion and ligand **1** was titrated with 0.100 M NaOH solution. The pink color of the cobalt(II) ion gave way to yellowish or brownish color during addition of the ligand or with initial addition of NaOH. During the titration and increase of pH the solutions darkened. Attainment of equilibria became very slow (more than 15–30 min) by the pH range 3.67–4.73. At the end of the titration the solutions were yellowish or dark brown. On standing overnight they became slightly darker and the yellow color weakened. No precipitation from the solutions was observed.

SUPERQUAD analysis showed that only two deprotonated complexes, Co(HL)L<sup>+</sup> and Co(HL)<sub>2</sub>L<sup>+</sup>, were formed in addition to the three complexes Co(HL)<sub>r</sub><sup>2+</sup> with  $r=1, 2$  and  $3$ . The fit to the experimental data was unsatisfactory:  $\chi^2=32.0$  and  $s=3.92$ . The  $Z_H$  curves (figure 1) did not exceed the zero level, showing that the deprotonated complexes were not formed in large amounts. The high  $Z_H$  values of the 1:1 titrations point to the presence of protonated complexes with H<sub>2</sub>L<sup>+</sup> as ligand. SUPERQUAD analysis showed that only the protonated complex with  $pqr$  combination 123 with tentative formula Co<sub>2</sub>(HL)<sub>2</sub>H<sub>2</sub>L<sup>5+</sup> exhibits satisfactory fit ( $\chi^2=6.55$ ,  $s=1.73$ ; 202 data points from 6 titrations) to the experimental data. Because the stable pH ranges were very narrow, the lower limit for calculation of the stability constants was chosen to be 1.80, where in spite of the high liquid junction potential the weighting coefficients of the titration points were small (in general between +3.0 and -3.0). Stability constants are given in table 1. SUPERQUAD analysis rejected all the deprotonated polynuclear complexes. An example of the concentration distribution

Table 1. Proposed formulae and stability constants for pyridine oxime complexes relating to the reaction  $p\text{H}^+ + q\text{Co}^{2+} + r\text{HL} \rightleftharpoons (\text{H}^+)_p(\text{Co}^{2+})_q(\text{HL})_r$  in aqueous 0.1 M NaCl solution at 25°C.<sup>a</sup>

<i>p</i>	<i>q</i>	<i>r</i>	Proposed formula	log β <sub>pqr</sub>				
				Ligand 1	Ligand 2	Ligand 3	Ligand 4	Ligand 5
0	1	1	Co(HL) <sup>2+</sup>	3.94 ± 0.01	2.56 ± 0.02	2.85 ± 0.01	3.74 ± 0.03	1.19 ± 0.06
0	1	2	Co(HL) <sub>2</sub> <sup>2+</sup>	7.51 ± 0.01	4.73 ± 0.02	5.04 ± 0.02	7.04 ± 0.10	
0	1	3	Co(HL) <sub>3</sub> <sup>2+</sup>	10.44 ± 0.02				
-1	1	2	Co(HL) <sub>2</sub> L <sup>+</sup>	2.44 ± 0.07	-1.87 ± 0.05	0.43 ± 0.10	4.27 ± 0.05	
-2	1	2	CoL <sub>2</sub>			-4.92 ± 0.08		-9.78 ± 0.08
-1	1	3	Co(HL) <sub>2</sub> L <sup>+</sup>	5.10 ± 0.10		3.14 ± 0.06		
-3	2	2	Co <sub>2</sub> L <sub>2</sub> OH <sup>+</sup>					-14.81 ± 0.04
-3	2	3	Co <sub>2</sub> L <sub>3</sub> <sup>+</sup>					-11.39 ± 0.03
-4	2	3	Co <sub>2</sub> L <sub>3</sub> OH					-19.12 ± 0.03
1	1	1	Co(H <sub>3</sub> L) <sup>3+</sup>		5.97 ± 0.17			
1	2	3	Co <sub>2</sub> (HL) <sub>2</sub> H <sub>2</sub> L <sup>5+</sup>	16.22 ± 0.03				
1	0	1	H <sub>3</sub> L <sup>+</sup>	3.798	5.017	3.590	3.968	4.258
2	0	1	H <sub>3</sub> L <sup>2+</sup>		7.307			
-1	0	1	L <sup>-</sup>	-11.7 <sup>b</sup>	-12.3 <sup>b</sup>	-10.01	-10.87	-9.94

<sup>a</sup>The protonation constants of the free ligands (log β<sub>p01</sub>) used in SUPERQUAD calculations were taken from refs. 1 (ligands 1–2) and 2 (ligands 3–5). <sup>b</sup>Approximate values in Ref. 1.

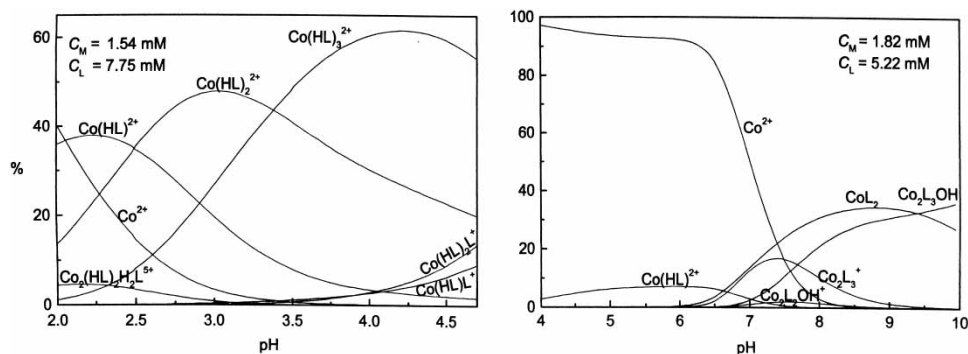


Figure 2. Examples of the concentration distribution of the cobalt(II) species vs pH for ligands 1 (left) and 5 (right).

of the cobalt(II) species is shown in figure 2. The computer program SPE [13] was used in these calculations.

### 3.2. The Co<sup>2+</sup>–ligand 2 system

The complexes formed by ligand 2 were clearly less stable than those formed by ligand 1. This is due to the CH<sub>2</sub> group of 2, which leads to six-membered chelate rings. Six-membered rings are less stable and are formed in higher pH ranges than five-membered ones. The formation of the cobalt(II) complexes could be followed to pH 6.0–6.2. Like solutions of ligand 1, these solutions too changed during titration from pink to yellow and finally to brown. Formation and oxidation of a low spin cobalt(II) complex was observed in the SUPERQUAD calculation. All the solutions with more

than two-fold excess of ligand led to large  $\chi^2$  and  $s$  values and had to be removed from the SUPERQUAD calculation, which was finally run with only three solutions. The best fit ( $\chi^2 = 7.87$ ,  $s = 1.28$ ; 124 data points from 3 titrations) was obtained with complexes  $\text{Co}(\text{H}_2\text{L})^{3+}$ ,  $\text{Co}(\text{HL})^{2+}$ ,  $\text{Co}(\text{HL})_2^{2+}$  and  $\text{Co}(\text{HL})\text{L}^+$ . Stability constants are given in table 1.

Addition of a solution with  $C_{\text{Co}}:C_{\text{L}} \approx 1:3$  to the three solutions included in the calculation led to unreliably high values of the stability constants especially for  $\text{Co}(\text{HL})_2^{2+}$  and  $\text{Co}(\text{HL})\text{L}^+$ , with  $\chi^2 = 82.6$  and  $s = 3.86$ . This was due to the increasing oxidation of low spin cobalt(II) to cobalt(III) complexes in the presence of excess ligand.

### 3.3. The $\text{Co}^{2+}$ –ligand 3 system

In the  $\text{Co}^{2+}$ –ligand 3 system seven solutions with initial  $C_{\text{L}} = 5.32$ – $8.10$  mM were titrated with 0.1 M NaOH using a very strong nitrogen flow and strong magnetic mixing. Five solutions with initial  $C_{\text{M}} = 1.82$ – $8.54$  mM could be titrated to pH 3.87–4.24, but solutions with very low metal ion concentrations ( $C_{\text{M}} < 0.4$  M) could be titrated to pH 10–11. The oxidation of low spin cobalt(II) complexes appeared to be strongest in the pH range 5–8, where only 0.02 cm<sup>3</sup> titrant at a time could be added, but oxidation was not marked in the pH range 9–11.

In all solutions the initial pink color weakened during the titration and gradually changed to an intense yellow. Hartkamp [14] reported a similar observation in that solutions of cobalt(II) obtain an intense yellow color upon addition of ligand 3. Overnight the solutions acquired a brownish tinge, but the basic yellow color persisted.

The  $Z_{\text{H}}$  curves show that complex formation is clear in the pH range 2–3, although weaker than with ligand 1. In the SUPERQUAD calculations, the pH range was limited to around 8.66, where the cobalt(II) ion was already completely present as  $\text{CoL}_2$ . The SUPERQUAD program rejected the stability constants  $\beta_{-111}$ ,  $\beta_{013}$ ,  $\beta_{-213}$  and  $\beta_{-313}$  when titration points in the pH range 9–11 were included. The best fit ( $\chi^2 = 39.5$ ,  $s = 1.59$ ; 297 data points from 7 titrations) was obtained by assuming the complexes  $\text{Co}(\text{HL})^{2+}$ ,  $\text{Co}(\text{HL})_2^{2+}$ ,  $\text{Co}(\text{HL})\text{L}^+$ ,  $\text{CoL}_2$  and  $\text{Co}(\text{HL})_2\text{L}^+$  with the stability constants given in table 1.

### 3.4. The $\text{Co}^{2+}$ –ligand 4 system

In all solutions of the  $\text{Co}^{2+}$ –ligand 4 system with variable compositions, the pink color of the cobalt(II) ion turned with the first NaOH additions to yellowish or brownish. The  $Z_{\text{H}}$  curves indicate strong complex formation in the pH range 1.7–2.0. Such low and narrow pH ranges (upper limits 2.7–2.9) pose difficulties for the determination of stability constants. The lowest pH limit to be used in the calculations was chosen as 1.80. SUPERQUAD calculations based on 129 data points from six solutions gave the best  $\chi^2$  and  $s$  statistics for the complexes  $\text{Co}(\text{HL})^{2+}$ ,  $\text{Co}(\text{HL})_2^{2+}$  and  $\text{Co}(\text{HL})\text{L}^+$  ( $\chi^2 = 12.58$  and  $s = 2.94$ ). Stability constants are given in table 1.

### 3.5. The $\text{Co}^{2+}$ –ligand 5 system

During titrations, solutions of the  $\text{Co}^{2+}$ –ligand 5 system took on a weak yellowish brown color, which intensified, and by the end of the titrations (pH 8–11) the solutions were often of a reddish tone. The  $Z_{\text{H}}$  curves with  $C_{\text{L}}/C_{\text{M}} = 2$ –5 (figure 1) have a plateau

in the pH range 7–9 and an inflection point at  $C_H \approx -2C_M$  indicating that the major species should be  $\text{CoL}_2$ ,  $\text{Co}_2\text{L}_2(\text{OH})_2$  or  $\text{Co}_2\text{L}_3\text{OH}$ , where  $p = -2q$ . The increases in the  $Z_H$  curves with low  $C_L/C_M (\leq 1)$  over the level  $Z_H = 1$  also indicate the existence of complexes with  $p < -r$ . The SUPERQUAD program calculated stability constants for complexes  $\text{Co}(\text{HL})_r^{2+}$ ,  $\text{CoL}_2$ ,  $\text{Co}_2\text{L}_2\text{OH}^+$ ,  $\text{Co}_2\text{L}_3^+$  and  $\text{Co}_2\text{L}_3\text{OH}$  ( $\chi^2 = 10.2$ ,  $s = 2.12$ ; 233 data points from 5 solutions), as given in table 1. An example of the concentration distribution of the cobalt(II) species in the solutions is given in figure 2.

### 3.6. Discussion

Slowing of the attainment of equilibrium in very low pH ranges is a clear indication of the formation of low spin cobalt(II) complexes, which are oxidized to cobalt(III) complexes. In high spin cobalt(II) complexes octahedral coordination ( $t_{2g}^5 e_g^2$ ) is most common, but the  $d^7$  structure also favors tetrahedral coordination with two fully occupied lower  $e$  and three half-occupied higher energy  $t_2$  orbitals ( $e^4 t_2^3$ ). There are always some tetrahedral and octahedral aqua ions in equilibrium in aqueous solution. The low spin state is generally encountered in cobalt(II) complexes where the energy level difference between  $t_{2g}$  and  $e_g$  orbitals is  $\Delta \approx 15\,000 \text{ cm}^{-1}$  ( $\approx 180 \text{ kJ mol}^{-1}$ ) [11].

All protonated cobalt(II) complexes with ligands **1–5**,  $\text{Co}(\text{HL})_r^{2+}$  ( $r = 1, 2$  or  $3$ ) were less stable than the corresponding nickel(II) complexes in agreement with the Irving–Williams stability order [15]. The stability constants generally increased in the ligand order  $\mathbf{5} < \mathbf{2} < \mathbf{3} < \mathbf{4} < \mathbf{1}$ . With a few exceptions the same order was observed for copper(II) [1,2], nickel(II) [1,3,4] and zinc(II) [5,6]. This, together with the normal stepwise stability orders  $K_1 > K_2 > K_3$ , indicates high spin states at least for the mono and bis complexes,  $\text{Co}(\text{HL})_r^{2+}$  and  $\text{Co}(\text{HL})_2^{2+}$ . Abnormal stability orders of  $K_3 > K_1 > K_2$  are known, for example, for the 2,2'-bipyridyl and 1,10-phenanthroline complexes  $\text{FeL}^{2+}$ ,  $\text{FeL}_2^{2+}$  and  $\text{FeL}_3^{2+}$ , where the aqueous mono and bis complexes are high spin but the tris complexes are low spin [16,17]. These ligands are comparable to the uncharged pyridine oximes **1** and **3–5** with similar coordination groups ( $-\text{N}=\text{C}-\text{C}=\text{N}-$ ). The stability orders for the aqueous cobalt(II) complexes with both 2,2'-bipyridyl and 1,10-phenanthroline are normal:  $K_1 > K_2 > K_3$  [17]. The Jahn-Teller distortion can cancel any possible stability enhancement by spin pairing, but the oxidation potential of the 1,10-phenanthroline complex  $\text{CoL}_3^{2+}$  is negative [18] ( $\text{CoL}_2^{2+} \rightleftharpoons \text{CoL}_3^{3+} + e^-$ ;  $E_0 = -0.18 \text{ V}$ ) indicating a high spin rather than a low spin state. For the complex  $\text{Co}(\text{HL})_3^{2+}$  of ligand **1**, the high concentrations (figure 2) without any observable oxidation also indicate a high spin state.

The deprotonated complexes  $\text{Co}(\text{HL})\text{L}^+$  and  $\text{Co}(\text{HL})_2\text{L}^+$  are undoubtedly low spin. This is inferred by the slowed attainment of equilibria soon after their appearance and by the fact that their parent complexes  $\text{Co}(\text{HL})_2^{2+}$  and  $\text{Co}(\text{HL})_3^{2+}$  are generally stronger acids, by 2–3 log units, than the corresponding nickel(II) and zinc(II) complexes [1–6]. The deprotonation of the ligand HL to  $\text{L}^-$  shortens the metal–ligand bonds and strengthens the ligand field around the  $\text{Co}^{2+}$  ion, thus causing the pairing of its unpaired spins.

The deprotonated bis complexes  $\text{Co}(\text{HL})\text{L}^+$  contain an intramolecular hydrogen bridge ( $=\text{N}-\text{O}-\text{H} \cdots \text{O}-\text{N}=\text{O}$ ) between the oxygen atoms of two *cis*-oriented oxime groups, as has been verified in several structures with comparable ligands [19,20]. The smaller ionic radius of the low spin cobalt(II) ion (65 pm) compared with that of high spin cobalt(II), nickel(II) and zinc(II) ions (73.5, 70 and 74.5 pm [21], respectively)



strengthens the intramolecular hydrogen bridge, the metal–ligand bonds in the deprotonated complexes, and also the acidity of their parent complex  $\text{Co}(\text{HL})_2^{2+}$ .

The stabilities of pyridine-2-acetamidoxime (**2**) complexes are weakened by their six-membered chelate rings. At low pH ranges the ligand additionally forms with cobalt(II) ion the complex  $\text{Co}(\text{H}_2\text{L})^{3+}$  with  $\log \beta_{111} = 5.97 \pm 0.17$  and  $\text{p}K_{a1} \approx 3.4 \pm 0.1$ . Analogous complexes are also formed by 3-aminopropanamidoxime and its *N*-methyl derivatives with cobalt(II) [22] and copper(II) ions [23]. The structure of these ligands allows the positively charged pyridinium or ammonium groups to be situated sufficiently far from the central metal ion.

In the binuclear complex  $\text{Co}_2(\text{HL})_2\text{H}_2\text{L}^{5+}$  ligand **1** is in the form  $\text{H}_2\text{L}^+$  as well as HL. The structure of this complex is very difficult to predict. Probably it involves a combination of  $\text{Co}(\text{HL})^{2+}$ ,  $\text{Co}(\text{HL})_2^{2+}$  and a proton  $\text{H}^+$  that connects the complex nuclei with a hydrogen bridge. The bridge is broken by the deprotonation of  $\text{H}_2\text{L}^+$  to HL. The concentration of  $\text{Co}_2(\text{HL})_2\text{H}_2\text{L}^{5+}$  reaches its maximum value in the pH range 1.7–2.1 (figure 2).

With ligand **3** the only observed tris complex,  $\text{Co}(\text{HL})_2\text{L}^+$ , is displaced in the pH range 5–8 by  $\text{CoL}_2$ , which accounts for all the cobalt(II) present. The more deprotonated tris complexes  $\text{Co}(\text{HL})\text{L}_2$  and  $\text{CoL}_3^-$  are not observed even in the pH range 9–11. Bolton and Ellin [24], and, more clearly, Burger, Egyed and Ruff [25] found that Bjerrum plots ( $\bar{n}$  vs  $\log [\text{L}^-]$ ) of cobalt(II) solutions with **3** approach the limiting value 2.0 (calculated over the zero level  $\text{L}^-$ ,  $\text{H}_2\text{O}$  and  $\text{Co}^{2+}$ ). Both research teams [24,25] observed complexes  $\text{FeL}_3^-$  and  $\text{NiL}_3^-$  but not  $\text{Co}(\text{HL})\text{L}_2$  or  $\text{CoL}_3^-$ .

With ligands **1–4** the acid constants of the bis and tris complexes of types  $\text{M}(\text{HL})_2^{2+}$  and  $\text{M}(\text{HL})_3^{2+}$  generally increase in the order  $\mathbf{2} < \mathbf{1} < \mathbf{4} < \mathbf{3}$  [1–4]. This is also the acidity order of the oxime NOH groups of the free ligands [1–3]. The bis and tris complexes of ligands **3** and **4** are generally stronger acids by 2–3 log units than the corresponding complexes of ligands **1** and **2** [1–6]. As an exception, the bis complex  $\text{Co}(\text{HL})_2^{2+}$  of **3** ( $\text{p}K_a \approx 4.61$ ) is a weaker acid by about 2 log units than  $\text{Co}(\text{HL})_2^{2+}$  of **4** ( $\text{p}K_a \approx 2.77$ ). The deprotonated bis complex  $\text{Co}(\text{HL})\text{L}^+$  of **3** seems to be high spin in aqueous solution at least for the most part, but the complex  $\text{Co}(\text{HL})\text{L}^+$  of **4** is low spin. Ligand **3** clearly forms somewhat weaker ligand fields than ligands **1**, **2** and **4**. However, the complexes  $\text{CoL}_2$  and  $\text{FeL}_3^-$  of ligand **3** are low spin. Burger, Egyed and Ruff [25] have observed with qualitative NMR measurements [26] that in aqueous solution the complex  $\text{CoL}_2$  is only weakly paramagnetic,  $\text{FeL}_3^-$  is completely diamagnetic and  $\text{NiL}_3^-$  is equally paramagnetic to the aqua ion  $\text{Ni}^{2+}$ .

Additionally with ligand **4**, the formation of complexes  $\text{Co}(\text{HL})^{2+}$  and  $\text{Co}(\text{HL})_2^{2+}$  is already strong in the pH range 1.7–2.0. The deprotonation of the strongly acidic  $\text{Co}(\text{HL})_2^{2+}$  to the easily oxidizable low spin complex  $\text{Co}(\text{HL})\text{L}^+$  leads to slow attainment of equilibrium in the pH range 2.5–2.9. Ligand **4** evidently forms tris complexes also with cobalt(II), as with the nickel(II) ion [4], but with  $\log \beta_{013} \approx 9.0$ –9.5 (estimated), complex  $\text{Co}(\text{HL})_3^{2+}$  does not comprise more than 2–5% of  $C_M$ , before the slow attainment of equilibrium begins in the pH range 2.7–2.9.

The weaker tendency of **5** toward 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, e.g., with methylated pyridine [27–29] and 2-picolinate ligands [30]. With large metal ions like  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ , in contrast, the increased basicity of the ligand due to the presence of the methyl group may actually lead to stabilization of complexes.

Such is the case, for example, with 6-methyl-2-picoline [30] and with tetrahedral copper(I) complexes of 2-picoline [28,29].

The main species  $\text{CoL}_2$  of ligand **5** in the presence of excess ligand in the pH range 6–9 (figure 2) is undoubtedly low spin. Because of Jahn-Teller distortion, its oximato groups are located in the  $xy$  plane with *trans* orientation (the 6-methyl groups cause steric interference with *cis* orientation [2,4–6]). In the binuclear complexes  $\text{Co}_2\text{L}_3^+$  and  $\text{Co}_2\text{L}_3\text{OH}$ , one of the cobalt(II) ions is in a  $\text{CoN}_4\text{O}_2$  environment and the other in a  $\text{CoN}_2\text{O}_4$  environment. The cobalt(II) ions in  $\text{Co}_2\text{L}_3\text{OH}$  are evidently linked together via two oximato bridges and a hydroxo bridge with *fac* orientation to both cobalt(II) ions. The crystalline metallocrown [31]  $[\text{Ni}_9\text{L}_{10}(\text{OH})_6(\text{H}_2\text{O})_6](\text{ClO}_4)_2(10\text{H}_2\text{O})$  contains similarly linked nickel atoms in adjacent  $\text{NiN}_4\text{O}_2$  and  $\text{NiN}_2\text{O}_4$  environments (forming  $\text{Ni}_2\text{L}_3\text{OH}$  units) [4,32]. However, in aqueous (0.1 M NaCl) solution the major species are  $\text{Ni}_2\text{L}_3^+$  and (at higher pH ranges)  $\text{Ni}_3\text{L}_3(\text{OH})_3^+$ , the complex  $\text{Ni}_2\text{L}_3\text{OH}$  cannot be observed at all, and the amounts of  $\text{NiL}_2$  remain small [4]. The tendency of cobalt(II) to form low spin complexes increases the stabilities of  $\text{CoL}_2$  and  $\text{Co}_2\text{L}_3\text{OH}$ . In  $\text{Co}_2\text{L}_2\text{OH}^+$ , both cobalt(II) ions are in  $\text{CoN}_2\text{O}_4$  environments and are evidently high spin, and the amounts of  $\text{Co}_2\text{L}_2\text{OH}^+$  remain small (figure 2). In the pH range 9–10,  $\text{Co}_2\text{L}_3\text{OH}$  becomes the main species, although one of its three oximato ligands must lie, because of steric requirements, in the  $z$  axis of the low spin cobalt(II) ion in the  $\text{CoN}_4\text{O}_2$  environment or, because of Jahn-Teller distortion, at an angle to it. The other cobalt(II) ion is in a  $\text{CoN}_2\text{O}_4$  environment and is probably high spin.

The formation of  $\text{Co}_2\text{L}_3^+$  and  $\text{Co}_2\text{L}_3\text{OH}$  evidently originates from the tendency of cobalt(II) to complete its octahedral coordination sphere with ligand **5**. This is an essential difference between ligand **5** and ligand **3**, which forms quantitatively the complex  $\text{CoL}_2$  in the pH range 9–10. The 6-methyl group has the decisive effect. We have noted earlier [33] that the 2-aminoacetamidoxime and 2-(methylamino)acetamidoxime complexes  $\text{Ni}(\text{HL})\text{L}^+$  are also square-planar (with the same characteristic orange color) both in the solid state and in aqueous solution but the corresponding 2-(dimethylamino)acetamidoxime complex is octahedral in aqueous solution. It is possible that the complex  $\text{CoL}_2$  of **3** is at least partly square-planar in aqueous solution. The comparable dimethylglyoxime complex  $\text{Co}(\text{dmg})_2$  is square-planar in the solid state, but in aqueous solution it is able to form mixed halide or pseudohalide complexes  $\text{Co}(\text{Hdmg})(\text{dmg})\text{X}_n^{1-n}$  or  $\text{Co}(\text{dmg})_2\text{X}_n^{n-}$  ( $n = 1$  or  $2$ ) [34]. The coordination of chloride, bromide [34] and iodide [35] ions decreases with increasing water activity (with decrease of concentrations of alkali metal salts used as background electrolytes and in the order  $\text{Li}^+ > \text{Na}^+ > \text{Rb}^+$ ), evidently owing to the increasing coordination of aqua ligands along the  $z$  axis of  $\text{Co}(\text{dmg})_2$  [34,35].

As noted above, in the system involving ligand **3** only solutions of very low  $C_M$  ( $< 0.4$  mM) could be titrated over the pH range 5–10. With ligand **5** solutions with much higher  $C_M$  (1–8 mM, figure 1) could be titrated over the pH range 7–10. Hartkamp [14] reported that solutions of the 6-methylpyridine-2-aldoxime (**5**) complexes  $\text{Cu}(\text{HL})_2^+$  and  $\text{CuL}_2^-$  are stable for at least 24 hours in the presence of air and hydroxylamine, whereas all the pyridine-2-aldoxime (**3**) [14], pyridine [28] and 2-, 3- and 4-picoline [29] complexes of copper(I) are rapidly oxidized in the presence of air to copper(II) complexes. The 6-methyl groups of ligand **5** clearly protect the copper(I) and low spin cobalt(II) ions in tetrahedral and octahedral coordination environments against oxidation. The square-planar or square-pyramidal cobalt(II)

complexes should be more sensitive to attacks along the  $z$  axis, so the  $\text{CoL}_2$  complex of **5** is probably octahedral.

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