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Coordination Compounds of N-(2-aminophenyl)- and N-(3-aminophenyl)pyridine-2′-carboxamide with Cobalt(II) and Cobalt(III). The Nature of Amide Deprotonation Induced by Cobalt(III) in Acidic *pH*

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New complexes of the general formulae $CoL_2X \cdot n\,H_2O$ (X = Cl, Br, I, NCS, NO_3 and n = 0, 1, 2 or 3), $Co_2L_2X_3 \cdot Et$OH (X = Cl, Br, I, NCS), $Co(DH)X_2$ (X = NCS, NO_3) and $Co(DH)_2X_2$ (X = NCS, I) have been prepared, where LH = N-(2-aminophenyl)pyridine-2′-carboxamide and DH = N-(3-aminophenyl)pyridine-2′-carboxamide. The compounds were characterized by X-ray powder patterns, conductivity measurements, thermogravimetric analysis, magnetic properties as well as by IR, ligand field and ^{1}H-NMR spectroscopy. In the presence of oxygen, LH undergoes a cobalt(III) ion promoted amide hydrogen ionization in the *pH* region 4–6.

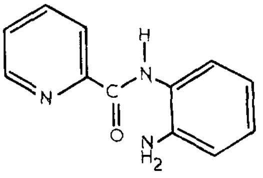
[Keywords: Amide deprotonation; Cobalt(II) complexes; Cobalt(III) complexes; Electronic spectra; IR; Magnetic moments]

Koordinationsverbindungen von N-(2-aminophenyl)- und N-(3-aminophenyl)pyridin-2′-carboxamid mit Cobalt(II) und Cobalt(III). Die Natur der Deprotonierung von Amiden induziert von Cobalt(III) in saurem Medium

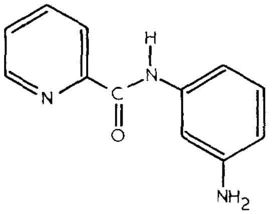
Neue Komplexe der allgemeinen Formeln $CoL_2X \cdot n\,H_2O$ (X = Cl, Br, I, NCS, NO_3 und n = 0, 1, 2, 3), $Co_2L_2X_3 \cdot Et$OH (X = Cl, Br, I, NCS), $Co(DH)X_2$ (X = NCS, NO_3) und $Co(DH)_2X_2$ (X = NCS, I) wurden dargestellt mit LH = N-(2-aminophenyl)pyridin-2′-carboxamid und DH = N-(3-aminophenyl)pyridin-2′-carboxamid. Die Verbindungen wurden mittels Röntgenstrukturanalyse, Leitfähigkeitsmessungen, thermogravimetrischen Analysen, magnetischen Eigenschaften sowie mit IR-, Ligandenfeld- und ^{1}H-NMR-Spektroskopie charakterisiert. In Gegenwart von Sauerstoff unterliegt LH einer Cobalt(III)ion-induzierten Amidwasserstoffionisierung im *pH*-Bereich 4—6.

Introduction

The inorganic chemistry of organic amides is an important part of a number of current chemical problems[1–3]. The main results on the coordinating properties of the amide bond were reviewed by *Sigel* and *Martin*[1]. Their survey clearly shows that research interest is centred on the stability and structure of metal ion complexes of amides, oligopeptides and related ligands; of special interest are the deprotonation processes and the species thereby formed. As part of our systematic investigation of the metal-amide interactions[4–11], we report here the preparation and study of complexes of Co(II) and Co(III) salts with N-(2-aminophenyl)pyridine-2′-carboxamide (**A**) and N-(3-aminophenyl)pyridine-2′-carboxamide (**B**), abbreviated as *L*H and *D*H, respectively. These ligands have interesting ligating possibilities because they have three donor groups, two of which (the aromatic amino group and the pyridine N-atom) may serve as anchoring groups[1] to the secondary amide bond favoring deprotonated products. *L*H and *D*H have been shown to coordinate to Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pd(II) and Pt(II) in several modes[9–11], largely determined by the nature of the metal ion, the *o*- or *m*-position of the $-NH_2$ group and the *pH* of the reaction system. Particular attention is devoted to the cobalt ion-amide systems because a) deprotonation of the amide hydrogen and coordination of Co(II) at the amide nitrogen appear essential for oxygenation of dipeptide complexes[1], b) the N-coordination of the deprotonated amide bond leads to the lowering of reduction potentials of metal couples, i.e., stabilization of high oxidation states[2], c) some preliminary results reported in Ref.[9] supported evidences for unusual stoichiometries, and d) Co(II) was reported to be the first and only metal ion which promotes amino proton ionization near the physiological *pH* range[12,13].



A



B

Experimental

The ligands were obtained as described previously[9]. Analyses and physicochemical techniques were carried out by published methods[9,14]. The *pH* of the reaction mixtures was followed by an Orion Research (model 801 A) *pH*-meter with glass and calomel electrodes. The complexes $\mathrm{Co}L_2X\cdot n\,\mathrm{H_2O}$ ($X=$ Cl, Br, I, NCS, $\mathrm{NO_3}$ and $n = 0$, 1, 2 or 3) were prepared by adding a solution of LH (14 mmol) in absolute ethanol (180 ml) to a solution of 14 mmol of the required Co(II) salt [$\mathrm{CoCl_2}$, $\mathrm{CoBr_2}$, $\mathrm{CoI_2}$, $\mathrm{Co(NCS)_2}$, $\mathrm{Co(NO_3)_2\cdot 6\,H_2O}$] in water (40 ml). The reaction mixtures were heated under vigorous stirring at 50 °C in the atmosphere for 5 h and then allowed to stand at room temperature overnight. During the period of heating the initial pink colors of the solutions became at first brown and then wine to dark red; finally solid products separated out. The precipitates were collected by filtration, washed with ethanol (3 × 10 ml) and dried in vacuum over silica gel and sodium hydroxide. Using only absolute ethanol as solvent and strictly anhydrous Co(II) salts, the above synthetic procedure gave the complexes $\mathrm{Co_2}L_2X_3\cdot Et\mathrm{OH}$ ($X=$ Cl, Br, I, NCS). Immediately after the addition of the solution of LH to the solution of the metal salt, a dark green reaction mixture was obtained; no other color changes were observed. Efforts to prepare the analogous nitrato complex using $\mathrm{Co(NO_3)_2\cdot 6\,H_2O}$ as starting material and triethyl orthoformate for dehydration failed. A solid product with poor analytical results was obtained. When the *pH* of the above mentioned reaction mixtures was adjusted in the 7–10 region, hydroxo-derivatives of uncertain nature were isolated. The non-deprotonated complexes of *D*H were easily prepared by mixing and stirring a warm solution of $\mathrm{Co(NCS)_2}$, $\mathrm{CoI_2}$ or $\mathrm{Co(NO_3)_2\cdot 6\,H_2O}$ in absolute ethanol and few ml of triethyl orthoformate with the appropriate amount of the ligand dissolved in the minimum required hot volume of the same solvent. Solid product formation was instantaneous. The precipitates were collected, washed and dried as above. In the case of $\mathrm{Co(NCS)_2}$ two different complexes were obtained. Using 9.38 mmol of ligand and 9.45 mmol of the metal salt the compound $\mathrm{Co}(D\mathrm{H})(\mathrm{NCS})_2$ was prepared, while using a 2 : 1 or larger ligand : metal ion molar ratio $\mathrm{Co}(D\mathrm{H})_2(\mathrm{NCS})_2$ was isolated. It is worth noting that attempts to prepare the 1 : 1 iodide complex or the 2 : 1 nitrato compound, using various molar ratios and different reaction times, were also made, but in all experiments the complexes $\mathrm{Co}(D\mathrm{H})_2\mathrm{I}_2$ and $\mathrm{Co}(D\mathrm{H})(\mathrm{NO_3})_2$ were again precipitated. No evidence was obtained in any of the experiments for hydrolysis occurring at the amide group.

Results and Discussion

Preparative and analytical data, colors and molar conductivity values are given in Table 1. The complexes are microcrystalline or powder-like, stable in atmospheric conditions, insoluble in nonpolar solvents and soluble only in *DMF* and *DMSO*. The Λ_M values of the complexes **1**–**9** in *DMF* and *DMSO* are in accord with 1 : 1 electrolytes[15]. The fact that the conductivities of the solutions of **10**–**13** increase with time can be attributed to the strong donor capacity of the solvents used, which leads to displacement of anionic ligands and change of electrolyte type[15]; thus the data are somewhat difficult to interpret. X-ray powder diffraction patterns indicate that each compound represents a definite complex and not merely mixtures of simpler stoichiometric types. The data also indicate the formation of two series of isomorphous compounds corresponding to the formulae $\mathrm{Co}L_2X\cdot\mathrm{H_2O}$ ($X=$ Cl, Br) and $\mathrm{Co_2}L_2X_3\cdot Et\mathrm{OH}$ ($X=$ Cl, Br, I). Thermogravimetric (TG) and differential thermogravimetric (DTG)

Table 1. *Colors, pH of precipitation, yields, analytical results*[a]

No.	Complex	Color	*pH* of Precipitation	Yield (%)
1	$CoL_2Cl \cdot H_2O$	dark red	4.0–4.5	68[b]
2	$CoL_2Br \cdot H_2O$	dark red	4.5–5.0	74[b]
3	$CoL_2I \cdot 3\,H_2O$	red-brown	5.5–6.0	75[b]
4	$CoL_2(NCS) \cdot 2\,H_2O$	red-brown	4.5–5.0	30[b]
5	$CoL_2(NO_3)$	red	5.0–5.5	73[b]
6	$Co_2L_2Cl_3 \cdot EtOH$	dark green	3.5–4.0	76[c]
7	$Co_2L_2Br_3 \cdot EtOH$	olive green	4.0–4.5	78[c]
8	$Co_2L_2I_3 \cdot EtOH$	brown-green	5.5–6.0	61[c]
9	$Co_2L_2(NCS)_3 \cdot EtOH$	dark green	4.0–4.5	62[c]
10	$Co(DH)(NCS)_2$	bluish-green	6.5–7.0	94[c]
11	$Co(DH)_2(NCS)_2$	pink	6.5–7.0	68[c]
12	$Co(DH)_2I_2$	pale brown	6.5–7.0	95[c]
13	$Co(DH)(NO_3)_2$	deep red	6.5–7.0	84[c]

[a] Required values in parentheses.
[b] Based on the ligand.
[c] Based on the metal.

studies show that the water in the Co(III) complexes is lattice held[11], while the ethanol molecule present in **6**–**9** is coordinated.

The principal IR bands of interest are listed in Tables 2 and 3. In the ν(O—H) region the spectra of the hydrated complexes exhibit, on top of the strong $\nu(NH_2)$ bands, a weak, very broad absorption covering the whole 3 500–3 150 cm^{-1} region, attributed to the presence of exclusively lattice water[16]. The presence of coordinated ethanol ligand in **6**–**9** is manifested by a sharp ν(O—H) band at 3 510–3 455 cm^{-1} [17]. In the spectra of **1**–**9** large frequency decreases (95–190 cm^{-1}) for the $\nu(NH_2)$ bands and about 35 cm^{-1} for the $\delta(NH_2)$ band indicate —NH_2 coordination[18]. As would be expected from the stoichiometries the $\nu(N—H)_{amide}$ band is absent in **1**–**9**. The absence of large systematic shifts of the $\nu_{as}(NH_2)$, $\nu_s(NH_2)$, $\delta(NH_2)$ and $\nu(N—H)_{amide}$ bands in the spectra of the non-deprotonated Co(II) complexes of *D*H implies that there are no interactions between the amino group, amide-N atom and Co(II). The data for the deprotonated L^- complexes reveal that the amide I, II and III bands shift towards the region expected for amide-N coordination[19]. The amide II and III bands are replaced by a strong absorption at about 1 390 cm^{-1}, which is assigned to a pure C—N stretch; this frequency value is typical for deprotonated secondary amide complexes[19]. The shifts of these modes in the spectra of **10**–**13** indicate amide-O coordination[9, 19]. In the spectra of *and conductivity data for the prepared complexes*

X%	C%	H%	N%	Λ_M^d (S cm^2 mol^{-1})	
				DMF	*DMSO*
5.97 (6.60)	53.12 (53.69)	4.15 (4.14)	15.07 (15.66)	60	42
13.61 (13.74)	50.15 (49.58)	3.84 (3.82)	14.69 (14.46)	70	34
18.93 (19.10)	43.27 (43.39)	3.79 (3.95)	12.22 (12.65)	64	39
9.83 (10.06)	52.61 (51.99)	3.92 (4.16)	16.49 (16.98)	70	32
	52.49 (52.85)	3.61 (3.70)	18.13 (17.98)	69	40
15.11 (15.31)	45.08 (44.94)	3.81 (3.78)	11.84 (12.10)	50	30
28.62 (28.94)	37.40 (37.71)	2.97 (3.17)	10.11 (10.15)	72	37
38.97 (39.28)	32.45 (32.22)	2.91 (2.71)	9.00 (8.67)	65	39
22.50 (22.85)	46.14 (45.67)	3.23 (3.44)	16.79 (16.53)	67	36
29.30 (29.91)	42.82 (43.30)	3.13 (2.86)	17.90 (18.04)	58[e]	48[e]
19.99 (19.31)	51.43 (51.90)	3.44 (3.69)	18.04 (18.63)	64[e]	66[e]
33.93 (34.33)	38.86 (38.99)	3.09 (3.01)	11.36 (11.37)	120[e]	62[e]
	36.21 (36.37)	2.92 (2.80)	17.41 (17.68)	12[e]	8[e]

[d] Values of molar conductivity for ca. 10^{-3} *M* solutions at 25 °C.

[e] The conductivities of the solutions increase with time. X = Cl, Br, I, NCS; *Et*OH = ethanol.

all the complexes prepared the pyridine deformation bands shift to higher frequencies indicating coordination of the ring N-atom[20]. The spectra of **9**, **10**, and **11** exhibit the ν(CN) and δ(NCS) bands in the regions characteristic of terminal N-bonded isothiocyanate groups[21]. The frequencies of these modes in **4** support the presence of ionic thiocyanate[21]. The appearance of a strong band at 1 375 cm^{-1} in the spectrum of **5** confirms that an ionic D_{3h} nitrate group is present[22]. The values of the frequencies assigned as vibrational modes of the nitrate groups in **13** (Table 3) are strongly indicative of the presence of chelated bidentate nitrates[22, 23], because the separation of the two highest frequency bands is 190 cm^{-1}. In addition, the spectrum exhibits two strong ν (Co^{II}—O) bands in the far-IR region[23]. The possibility of bridging nitrato groups can be ruled out, because the highest frequency IR mode appears below 1 500 cm^{-1}[22]. The far-IR spectra of the complexes $Co_2L_2X_3 \cdot Et$OH (X = Cl, Br, I, NCS) and Co(DH)(NCS)$_2$ show terminal stretching Co(II)-X frequencies in the region expected for pseudotetrahedral coordination around Co(II)[24, 25].

The ^{1}H-NMR signal due to the amide proton is absent in the spectra of the diamagnetic Co(III) complexes (Table 4), providing conclusive evidence that this proton is lost during complexation. NMR evidences for iminol structures[26] were not found. The spectra show characteristic

Table 2. *Diagnostic IR ligand bands* (*cm*$^{-1}$)[a] *of N-(2-aminophenyl)pyridine-2'-* *cobalt(III) and cobalt*

Comp.	$\nu_{as}(NH_2)$[b]	$\nu_s(NH_2)$[c]	$\nu(N—H)_{amide}$	$\delta(NH_2)$[d]
*L*H	3410 s	3340 m	3310 m	1650 m
1	3310 s	3165 m		1620 m
2	3315 s	3160 m		1622 s
3	3315 mb	3190 m		1626 s
4	[i]	3185 m		1623 s
5	3300 mb	3205 s		1622 s
6	3295 s	3210 m		1620 m
7	3220 s	3150 mb		1625 m
8	3230 s	3190 mb		1619 s
9	3245 m	3190 m		1620 m
*D*H	3420 s	3345 s	3320 s	1640 s
10	3410 m	3325 m	3245 m	1641 sh
11	3415 s	3360 m	3285 sb	1642 s
12	3390 mb	3290 mb[j]	3290 mb[j]	1637 sh
13	3405 s	3335 mb	3305 m	1636 m

[a] Assignments of —NH_2 and amide bands for *L*H and *D*H were assisted by deuterium isotopic substitution.

[b] Antisymmetric stretching.

[c] Symmetric stretching.

[d] Scissoring.

[e] $\nu(C=O)$.

downfield shifts of the 6'-pyridyl and —NH_2 resonances relative to the free ligand, confirming the involvement of both the ring-N atom and the aromatic amino group in coordination[10, 27]. The integration ratio of the signals is consistent with the assignments.

Table 5 gives the room temperature magnetic moments and details of the solid state electronic spectra of the prepared complexes. Both the magnetic[28] and electronic spectral data[29] indicate that **10** has a pseudo-tetrahedral structure, while **11**, **12**, and **13** have high-spin six-coordinate configurations. Compounds **1**–**5** were shown (*Gouy* and *Faraday* methods) to be diamagnetic, confirming that they are Co(III) complexes. The frequencies of the observed absorption maxima and the values of the calculated ligand field parameters are in accord with the presence of a $[Co^{III}N_6]$ chromophore in the solid state[28, 29]. The solids formulated as $Co_2L_2X_3 \cdot Et$OH ($X =$ Cl, Br, I, NCS) have unusual magnetic and spectral properties. The effective magnetic moments found correspond very well to the average value for one low-spin cobalt(III) and one high-spin cobalt(II) *carboxamide, N-(3-aminophenyl)pyridine-2′-carboxamide and their cobalt(II), (II,III) complexes*

Characteristic I^e	Amide II^f		Bands III^f	$\delta(Py)^g$	$\delta(Py)^h$
1 680 vs	1 535 s		1 238 w	620 m	405 m
1 600 vs		1 389 vs		642 m	441 m
1 607 vs		1 388 vs		652 m	439 m
1 604 vs		1 401 vs		651 m	452 m, 444 sh
1 602 vs		1 386 vs		657 m	448 m
1 607 vs		1 395 vs		649 m	421 m
1 604 vs		1 388 vs		654 m	449 m
1 609 vs		1 393 vs		646 m	440 m
1 604 vs		1 401 vs		653 m	443 m
1 603 vs		1 394 vs		652 m	448 m
1 689 vs	1 549 s		1 241 m	620 m	402 m
1 623 vs	1 569 vs		1 265 s	645 m	418 w
1 621 vs	1 570 vs		1 269 m	652 m, 641 w	416 m
1 622 vs	1 568 s		1 270 m	652 m	411 w
1 625 vs	1 572 m		1 274 m	654 m	417 w

[f] These bands in secondary amides arise from ν (C—N) as well as from δ (NH) modes.

[g] In-plane pyridine ring deformation.

[h] Out-of-plane pyridine ring deformation.

[i] Not assigned.

[j] Overlapping.

atom per molecular unit. It seems likely that the diamagnetic subunit is the octahedral $[Co^{III}L_2]^+$ ion and that the paramagnetic one is the pseudotetrahedral $[Co^{II}X_3(EtOH)]^-$ ion; this is further supported by the solid state electronic spectra. These spectra contain bands at the same energies with those of the $[Co^{III}L_2]^+X^- \cdot n\,H_2O$ series (X = Cl, Br, I, SCN, NO_3) and maxima characteristic of pseudotetrahedral $[Co^{II}X_3L]^-$ anions (L = monodentate ligand) with C_{3v} symmetry[24, 25]. Square planar Co(II) structures, six-coordinate low-spin Co(II) configurations or d^7 spin-crossover situations can be ruled out with certainty[5, 9, 28, 29]; these stereochemistries exhibit maxima at different energies. Complexes with both Co(II) and Co(III) structural subunits have been characterized[30].

From the overall data presented it is concluded that *D*H acts as a bidentate chelate ligand through the amide-O and pyridine-N atoms. In **10** the tetrahedral coordination is completed by two monodenate isothiocyanate groups (**C**). The complexes **11**, **12**, and **13** have octahedral stereochemistries with $[Co^{II}O_2N_4]$, $[Co^{II}O_2N_2I_2]$ and $[Co^{II}O_5N]$ chro-

Table 3. *Characteristic IR inorganic anion and far-IR bands* (cm^{-1})

Complex	Thiocynate Bands[a]		Nitrate Bands[b]					$\nu(Co^{II} X)_t$
	ν(CN)	δ(NCS)	ν_3(E′)	$\nu_1(A_1)$	$\nu_4(B_2)$	$\nu_6(B_1)$	$\nu_3(A_1)$	
4	2 041 vs	471 m						
5			1 375 vs					
6								311 s, 285 m
7								244 vs, 223 vs
8								213 vs, 196 vs
9	2 062 vs	482 m						312 s, 296 m
10	2 070 vs	479 m						310 s, 295 m
11	2 075 vs	481 m						[c]
13				1 475 s	1 285 s	821 m	742 m	303 s, 292 vs

[a] The ν(CS) mode is obscured by the ligands' bands.

[b] The $\nu_2(A_1)$ and $\nu_5(B_2)$ modes of the C_{2v} nitrato groups were not assigned because the 990–1 050 and 690–720 cm^{-1} regions are obscured by strong bands of the coordinated ligand.

[c] Not assigned.

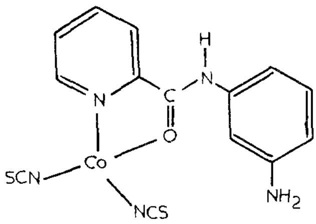
mophores, respectively. The cobalt(III) complexes **1**–**5** have octahedral stereochemistry with terdentate pyridyl-N, deprotonated amide-N and aromatic-NH_2 coordination of L^-(E). Deprotonation leads to systems having a considerable degree of delocalization. Synthetic, analytical, magnetic and spectroscopic data suggest that the complexes **6**–**9** are mixed-valence species and can be formulated as $[Co^{III}L_2]^+$ $[Co^{II}X_3(EtOH)]^-$. They contain the above mentioned bis-terdentate cobalt(III) cationic structural subunit and the $[Co^{II}X_3(EtOH)]^-$ pseudo-tetrahedral anionic one. The *iminol* structural type[26, 30], which seems to be an intermediate for deprotonated N-coordination of the amide bond, was not observed in the complexes studied.

Table 4. *Characteristic* ^{1}H-*NMR* *(δ, ppm)*[a, b] *spectral data of the diamagnetic cobalt(III) complexes in DMSO*-d_6

Complex	Water	NH (amide)	H_6-(pyridyl)	NH_2
*L*H		10.10 s	8.76 d	4.94 s
1	3.44 s		9.22 d	6.53 sb
2	3.41 s		9.09 d	6.37 sb
3	3.42 s		9.05 d	6.24 sb
4	3.47 s		9.03 d	6.26 sb
5			9.05 d	6.20 sb

[a] *TMS* was used as an internal standard.

[b] The spectra were ran immediately after dissolution. s = singlet; d = doublet; b = broad.



C

Since the discovery of metal ion induced amide (peptide) deprotonation reactions[31] several studies have led to the conclusion that only Pd(II), Cu(II), Ni(II), Co(II) and Zn(II) are usually capable of promoting these reactions. The promotion of amide hydrogen ionization increases in

Table 5. *Solid state magnetic moments and diffuse reflectence*

Complex	μ_{eff}[a, b] (BM)	Solid state[b] electronic spectra (10^3 cm^{-1})				
Low-spin octahedral Co(III) *complexes*		$^1A_{1g}\rightarrow$	$^1T_{2g}$,	$^1T_{1g}$,	$^3T_{2g}$,	$^3T_{1g}$
$[CoL_2]^+Cl^-\cdot H_2O$	dia		28.57	21.28	[c]	12.66
$[CoL_2]^+Br^-\cdot H_2O$	dia		28.98	21.14	[c]	13.33
$[CoL_2]^+I^-\cdot 3\,H_2O$	dia		29.07	21.27	14.71	12.58 sh
$[CoL_2]^+SCN^-\cdot 2\,H_2O$	dia		28.41	21.05	15.87	13.16
$[CoL_2]^+NO_3^-$	dia		28.49	21.20	17.33 sh	12.87
Co(II, III) *complexes*		Low-spin octahedral Co(III) structural unit				
		$^1A_{1g}\rightarrow$	$^1T_{2g}$,	$^1T_{1g}$,	$^3T_{2g}$,	$^3T_{1g}$
$[Co^{III}L_2]^+\,[Co^{II}Cl_3(EtOH)]^-$	2.27		28.73	21.27	[c]	12.61
$[Co^{III}L_2]^+\,[Co^{II}Br_3(EtOH)]^-$	2.29		29.15	21.19	[c]	12.63 sh
$[Co^{III}L_2]^+\,[Co^{II}I_3(EtOH)]^-$	2.39		28.56	21.05	16.66 sh	[c]
$[Co^{III}L_2]^+\,[Co^{II}(NCS)_3(EtOH)]^-$	2.22		29.37	20.41	[c]	13.33
Tetrahedral Co(II) *complex*		$^4A_2\rightarrow$	$^4T_1(P)$,		$^4T_1(F)$	
$[Co(DH)(NCS)_2]$	4.56		17.24 sh, 16.21		8.93, 7.87, 6.00	
High-spin octahedral Co(II) *complexes*		$^4T_{1g}\rightarrow$	$^4T_{1g}(P)$, $^4A_{2g}$,		$^4T_{2g}$	
$[Co(DH)_2(NCS)_2]$	5.18		20.83, 19.42, 18.51		9.21	
$[Co(DH)_2I_2]$	5.03		18.52, 15.63		7.90	
$[Co(DH)(NO_3)_2]$	4.69		19.21 sh, 18.40		8.71, 7.49	

[a] Per metal ion.
[b] At room temperature.
[c] Not observed.

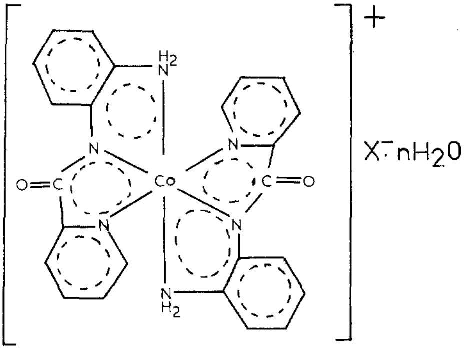
the series Zn(II) $\simeq$ Co(II) < Ni(II) < Cu(II) < Pd(II)[1]. Only the last three ions promote the deprotonation at $pH \leqslant 7$. It is worth noting that throughout most of the pH range, in the absence of metal ions, the amide group is neutral[1]. The ligand *L*H presents one of the most favorable cases for metal ion-promoted amide hydrogen deprotonation. The complex $ZnLCl\cdot H_2O$[11] was reported to be the first case of amide deprotonation induced by Zn(II) at $pH\,7$. The presence of two strong anchoring groups (pyridine N-atom and aromatic —NH_2 group), capable of forming two stable 5-membered chelate rings per L^- with the amide nitrogen, reduces the importance of metal ion hydrolysis; the full binding capabilities of the metal ion favour deprotonation. In addition the planarity of the amide group is maintained in the deprotonated trigonal amide nitrogen.

ligand field spectral data of the prepared complexes

		Spectral parameters[d]			
		D_q (cm^{-1})	B (cm^{-1})	C (cm^{-1})	β
		2 559	456	3 707	0.41
		2 504	490	3 905	0.44
		2 561	487	4 345	0.44
		2 499	460	3 945	0.41
		2 536	456	4 165	0.41
Tetrahedral Co(II) structural unit					
$^4A_2 \rightarrow$ $^4T_1(P)$,	$^4T_1(F)$				
16.00, 15.08 sh, 14.60	6.21, 5.81, 5.45	2 560 (332)	466 (707)	4 330	0.42 (0.73)
15.38, 14.55, 13.99	5.91, 5.23, 4.80	2 547 (305)	497 (693)	4 280	0.45 (0.71)
13.89	5.22, 4.77	2 512 (289)	469 (688)	4 071	0.42 (0.71)
17.02 sh, 16.06	8.38, 7.60, 6.82	2 395 (439)	560 (698)	3 540	0.50 (0.72)
		447	699		0.72
		1 038	811		0.84
		903	785		0.81
		918	765		0.79

[d] The values in parentheses correspond to the pseudotetrahedral $[Co^{II}X_3(EtOH)]^-$ structural subunit.

No evidence of Co(II) ion promoted amide hydrogen ionization appears at $pH \leqslant 7$ for both ligands studied. Using H_2O—*Et*OH solvent mixtures and in the presence of the atmospheric oxygen (but in the absence of molecular oxygen or activated charcoal), the reaction of *L*H with Co(II) salts leads to the formation of cationic Co(III) deprotonated complexes. The studied mechanism[1, 32, 33] in the case of analogous solution reactions with bis-dipeptide complexes indicates that the reaction is preceded by formation of a brown binuclear intermediate. The brown color was observed in our reaction mixtures before the precipitation of the red Co(III) solids. The binuclear indermediate may be viewed as an oxygenated complex of Co(II), but is best described as a peroxo complex of two Co(III) that is in facile equilibrium with oxygen and the initial mononuclear Co(II) species; the peroxo group occupies one coordination position on each Co(III) atom. In a second irreversible reaction peroxide is released, the coordination sphere is completed and the mononuclear



E (X=Cl, Br, I, SCN, NO_3)

Co(III) complex forms. The well-known inertness of Co(III) complexes accounts for the relatively large time of the reactions studied. Using absolute ethanol as solvent the mixed-valence Co(II, III) complexes **6–9** were isolated. We cannot offer a reliable explanation for this complication.

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