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First Anionic 1,10-Phenanthroline-2,9-dicarboxylate Containing Metal Complex Obtained from a Novel 1:1 Proton–Transfer Compound: Synthesis, Characterization, Crystal Structure, and Solution Studies

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The new 1,10-phenanthroline containing 1:1 proton–transfer compound **LH**$_2$, $[\text{pyda}\cdot\text{H}_2]^{2+}[\text{phendc}]^{2-}$, was synthesized from the reaction of 2,6-pyridinediamine, pyda, and 1,10-phenanthroline-2,9-dicarboxylic acid, phendc·H$_2$, and characterized by elemental analysis, ES–Ms, IR, ^{1}H, ^{13}C NMR, and UV/vis spectroscopies. Subsequently, the first example of $[\text{phendc}]^{2-}$ containing anionic complex $[\text{pyda}\cdot\text{H}]_2[\text{Co(phendc)}_2]\cdot 10\text{H}_2\text{O}$, was prepared, using the above novel proton-transfer compound, and structurally characterized by single-crystal X-ray diffraction. The complex crystallizes in the space group $P2_1/n$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 11.877(3)$ Å, $b = 31.473(9)$ Å, $c = 12.915(4)$ Å, and $\beta = 116.223(5)°$. The structure has been refined to a final value for the crystallographic R factor of 0.0524 based on 9021 observed independent reflections. The complexation reactions of pyda, phendc·H$_2$, and **LH**$_2$ with H$^+$ as well as **LH**$_2$ with Co(II) in aqueous solution were investigated by potentiometric pH titrations, and the equilibrium constants for all major complexes formed are described. The results are presented in the form of distribution diagrams revealing the concentrations of individual complex species as a function of pH. The results revealed that, at a pH range of 5.2–6.2, the major complex species is $[(\text{pyda}\cdot\text{H})]_2[\text{Co(phendc)}_2]$, similar to the isolated crystalline complex.

Introduction

1,10-Phenanthroline is a well-known N-heterocyclic chelating agent with a rigid planar structure. The metal chelating properties of 1,10-phenanthroline have been widely utilized in all aspects of coordination chemistry[1] as well as in its recent applications to develop biomimetic models of metalloenzymes[2] and to prepare supramolecules,[3] self-assembling systems,[4] or metal complexes with interesting anticancer properties.[5a,b]

1,10-Phenanthroline-2,9-dicarboxylic acid, phendc·H$_2$, has been widely employed as an appropriate intermediate in the synthesis of multidentate chelating agents with phenanthroline moieties.[6−8] The spectroscopic studies of the complexation of phendc·H$_2$ with Eu^{3+} has been reported.[9a] It has been introduced as a powerful sensitizing ligand for Eu^{3+} ion[9b,c] and an Eu^{3+} chelator in the sensitive measurement of molecules of biological interest, i.e., fibronectin, by time-resolved fluorescence spectrophotometry.[9c,d] It has also been applied in the preparation of antibodies with the ability to

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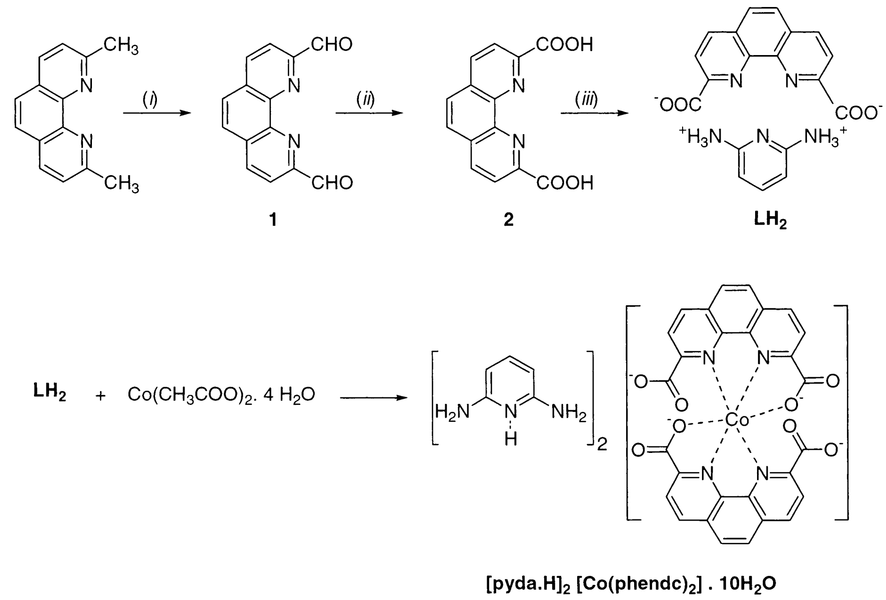
Scheme 1. Synthesis of LH_2 and $[pyda{\cdot}H]_2[Co(phendc)_2]{\cdot}10H_2O$ Complex[a]



[a] (i) SeO_2, 1,4-dioxane, reflux, 4 h; (ii) HNO_3 (60%), reflux, 3 h; (iii) 2,6-pyridinediamine, EtOH (95%), reflux, 90 °C, 20 min.

specifically recognize and measure UO_2^{2+}.[9e] To the best of our knowledge, despite some solution studies on the complexation of this ligand with metal ions, there is only one report on the crystal structure of its isolated Mg(II) complex.[10] The reported $[Mg(phendc)(H_2O)_3]{\cdot}2H_2O$ complex is a neutral complex in which one $[phendc]^{2-}$ anion participates in the complexation as a tetradentate ligand.

In this context it appeared of interest to synthesize a new $[phendc]^{2-}$ containing compound which may find general use for the preparation of novel metal−organic coordination compounds of 1,10-phenanthroline derivatives. Thus, the study was aimed by using 2,6-pyridinediamine, pyda, as a proper lewis base to produce a novel water-soluble proton-transfer compound, **LH**$_2$, (Scheme 1) acting as a suitable ligand for the preparation of the first example of $[phendc]^{2-}$ containing anionic complexes. This would enable us to assay the biologically in vitro and in vivo activities of the complexes as well as their interaction with DNA. Such activities have been known and reported for some of the metal complexes of 1,10-phenanthroline.[11]

To date, there have been several successful attempts at employing proton transfer from carboxylic acids to both heterocyclic and substituted amine nitrogens.[12,13] According to the "rule-of-thumb" presented by Etter,[14] in a system with a multitude of hydrogen-bonding functionalities, such as the 1:1 cocrystal of isonicotinamide and benzoic acid,[15] the best hydrogen-bond donor and the best hydrogen-bond acceptor will preferentially form hydrogen bonds to one another. Whenever the hydrogen bonding associations result in complete proton transfer to the nitrogen atom, an ionic compound is produced,[16] not a cocrystal. Recently, we reported a case in which a double proton transfer from 2,6-pyridinedicarboxylic acid, $pydc{\cdot}H_2$, to pyda resulted in the formation of a novel self-assembled $[pyda{\cdot}H_2]^{2+}[pydc]^{2-}$ system.[17] We, then, succeeded to use this self-assembled system in the preparation and characterization of Bi(III), Cr(III), Zn(II), Co(II), and Cu(II) complexes, some of which possess the $[pyda{\cdot}H]^+$ species as counterion and self-assemble into two or three dimensions via simultaneous ionic and hydrogen bonding interactions.[18] In general, molecular associations between carboxylic acids and Lewis bases result in more hydrogen−bonding associations with considerable stability upon a structure-making process which can be used in designing a novel layered crystalline material.[19]

In the present study, we demonstrate the application of the proton-transfer methodology in the preparation of the first example of a 1,10-phenanthroline containing anionic

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Co(II) complex using a novel proton-transfer compound **LH**$_2$, [pyda·H$_2$]$^{2+}$[phendc]$^{2-}$. The ionic **LH**$_2$ compound is potentially capable of forming self-assembled metal complexes. It could also be an interesting case of the supramolecular and foldamer chemistry[20] because of the presence of two bifunctional building blocks, pyda and phendc·H$_2$. The pyda contains two stereochemically suitable amine groups for interactive association via hydrogen bonding. This report also includes the solution studies of the complexation reactions of pyda and phendc·H$_2$ with H$^+$ and **LH**$_2$ with H$^+$ and Co(II).

Experimental Section

General Methods and Materials. IR spectra (200−4000 cm^{-1}) were recorded as KBr pellets or Nujol mulls using a Perkin-Elmer 843 spectrophotometer. ^{1}H and ^{13}C NMR were recorded on a Bruker DRX 500-Avance or Bruker AC-250 instruments. Chemical shifts are reported on the δ scale relative to tetramethylsilane (TMS). Electrospray mass spectra (ES-MS) were obtained using MS 80R FA and Varian Saturn 2000 GC MS spectrometers. Elemental analyses were carried out by Heraeus CHN-O-Rapid elemental analyzer. UV/vis spectra were recorded on a spectrometer—Philips PU 8750. Melting points were determined using an Electrothermal IA-9100 aparatus and are uncorrected.

All chemicals, except those mentioned, were obtained from commercial suppliers and used as received without further purification. The synthetic precursors, 1,10-phenanthroline-2,9-dicarboxaldehyde[21a] and 1,10-phenanthroline-2,9-dicarboxylic acid,[21b] were prepared according to the literature methods.

Proton-Transfer Compound LH$_2$, [pyda·H$_2$]$^{2+}$[phendc]$^{2-}$. This compound was prepared by refluxing the equimolar amounts of pyda and phendc·H$_2$ for 20 min at 90 °C in 95% ethanol, and the **LH**$_2$ compound was subsequently obtained by partial evaporation of the solvent at room temperature and recrystallization of the resulting cream compound from water. Mp: 222−224 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 5.87 (d, $J = 7$ Hz, H-3,5; py), 7.36 (t, $J = 7$ Hz, H-4; py), 8.14 (s, H-5,6; phen), 8.45 (d, $J = 7$ Hz, H-3,8; phen), 8.66 (d, $J = 7$ Hz, H-4,7; phen) ppm. ^{13}C NMR (DMSO−d$_6$): δ 95.04 (C-2,4; py), 124.05 (C-3; phen), 128.42 (C-5; phen), 130.53 (C-4a; phen), 138.24 (C-4; phen), 143.74 (C-4; py), 145.43 (C-10b; phen), 151.65 (C-2,6; py), 154.41 (C-2; phen), 168.73 (COO; phen) ppm. IR (Nujol): 3440−3250 (s), 3200 (m), 3080 (m), 2000−1800 (m), 1720 (m), 1695 (m), 1660 (m), 1600 (m), 1553 (w), 1500 (w), 1440 (s), 1405 (w), 1380 (s), 1350 (w), 1320−1295 (w), 1170 (m), 990 (w), 940 (w), 860 (m), 835 (m), 785 (m), 740 (m), 715 (s) cm^{-1}; (KBr): 636 (w), 607 (w), 560 (m), 427 (w), 360 (m), 300 (w) cm^{-1}. UV/vis: $\lambda_1 = 235.3$, $\lambda_2 = 285.6$, $\lambda_2 = 329.6$ nm. MS−ES, CH$_3$OH and NaCl as carriers, m/z: 110.0 [(pyda + H)$^+$], 131.9 [(pyda + Na)$^+$]. MS−ES, 0.2% formic acid in CH$_3$OH and CH$_3$CN as carrier, m/z: 173.0, 203.1, 214, 233.8, 269.2 [phendc·H$_3$]$^+$, 279.2, 331.0, 363.1, 388.3, 403.4, 425.4, 512.6, 590.1. Anal. Found (Calcd for C$_{19}$H$_{15}$N$_5$O$_4$·H$_2$O): C, 57.22 (57.72); H, 4.43 (4.33); N, 17.51 (17.71).

Table 1. Crystallographic Data for [pyda·H]$_2$[Co(phendc)$_2$]·10H$_2$O Complex

empirical formula	$C_{38}H_{48}CoN_{10}O_{18}$	β, deg	116.223(5)
fw	991.79	V, Å^3	4331(2)
space group	$P21/n$ (No.14)	Z	4
T, °C	−133	D_{calcd}, g cm^{-3}	1.521
λ (Mo Kα), Å	0.710 73	μ, mm^{-1}	0.486
a, Å	11.877(3)	$R1/wR2$ (obsd data)^a	0.0524/0.1295
b, Å	31.473(9)	$R1/wR2$ (all data)^a	0.0740/0.1448
c, Å	12.915(4)		

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0957P^2)]$; $P = (F_o^2 + 2F_c^2)/3$.

[pyda·H]$_2$[Co(phendc)$_2$]·10H$_2$O. A solution of Co(CH$_3$COO)$_2$·4H$_2$O (15.7 mg, 0.06 mmol) in water (10 mL) was slowly added to a stirring aqueous solution (50 mL) of **LH**$_2$ (50 mg, 0.13 mmol). Dark green crystals of the complex, suitable for X−ray analysis, were obtained by slow evaporation of the solution at room temperature. A few minutes after removing the crystals from the mother liquor, washing with distilled water, and drying in air, they would turn into a greenish powder. Yeild: 27 mg (44%). IR (KBr): 3383 (s), 3120 (s), 1680−1583 (s), 1565 (m), 1492 (w), 1458 (m), 1375 (s), 1308 (m), 1267 (w), 1200 (w), 1167 (m), 1125 (w), 975 (w), 867 (w), 840 (w), 800 (m), 783 (m), 712 (w), 648 (w), 617 (w), 583 (w), 560 (m), 480 (w), 432 (w), 375 (w), 333 (w), 283 (w) cm^{-1}. Anal. Found (Calcd for C$_{38}$H$_{28}$CoN$_{10}$O$_8$·6H$_2$O): C, 50.62 (49.63); H, 4.25 (4.38); N, 15.73 (15.23).

X-ray Structure Analysis. Analysis on prismatic dark green single crystals of [pyda·H]$_2$[Co(phendc)$_2$] ·10H$_2$O was carried out on a Bruker SMART CCD area detector diffractometer (Mo Kα radiation, graphite monochromator, $\lambda = 0.710\ 73$ Å) at −133 °C (140 K). Diffracted data were corrected for absorption using the SADABS program. Some softwares[22] including SMART (data collection), SAINT$^+$ (cell refinement and data reduction), SHELX-TL (version 5.10, structure solution & refinement; molecular graphics and publication material), and SHELXL-97 were used. A crystal of dimensions 0.3 × 0.3 × 0.4 mm^3 was mounted in a glass capilary, and the data were collected in the range $1.87 \le \theta \le 30.11°$, with $-16 \le h \le +16$, $-44 \le k \le +42$, $-18 \le l \le +18$. The structure was solved by direct method and refined by full-matrix least-squares based on F^2. The crytallographic data are listed in Table 1. The ORTEP diagram of the Co(II) complex represents the atoms by thermal ellipsoids drawn at the 50% probability level.

Potentiometric pH Titrations. All pH measurements were carried out with a model 632 digital pH meter equipped with a combined glass−calomel electrode. The base used for potentiometric pH titrations was carbonate free sodium hydroxide, which was standardized against primary standard oven-dried potassium hydrogen phthalate. A CO$_2$-free atmosphere for the base was ensured throughout. The potentiometric apparatus used consisted of a 50-mL glass jacketed cell, a constant-temperature bath (MLW thermostat, 25.0 ± 0.1 °C), a combined glass electrode, and a 10-mL capacity Metrohm piston buret, for which the tip was sealed in the cap of the titration cell with a clamp and O-rings. Atmospheric CO$_2$ was excluded from the titration cell with a purging steam of purified nitrogen gas. The electrodes were calibrated in the thermostated cell with standard acid−base to read pH directly (pH = −log [H$^+$]). The value of $K_w = [H^+][OH^-]$ used in the calculations was $10^{-13.78}$.[23] The concentrations of pyda, phendc·H$_2$, and **LH**$_2$ solutions were 2.0×10^{-3}, 8.0×10^{-3}, and $7.89 \times$

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10^{-4} M, respectively. A 9.446×10^{-2} M sodium hydroxide solution was used in the titrations of pyda and phendc·H_2, while a 7.844×10^{-2} M solution was applied in the case of **LH**$_2$. The ionic strength was adjusted to 0.1 M with $NaNO_3$. Before an experimental point (pH) was measured, sufficient time was allowed for establishment of equilibrium. Ligand protonation constants and its metal complexes' protonation, stability, and hydrolysis constants were calculated using the program BEST methods described by Martell and Motekaitis.[24]

Results and Discussion

Synthesis and Characterization of Proton-Transfer Compound, LH$_2$. The strategy adopted in the synthesis of **LH**$_2$ is outlined in Scheme 1. It involves the initial oxidation of neocuproin with SeO_2, to the corresponding dialdehyde **1**,[20a] followed by further oxidation with HNO_3 (60%) to prepare dicarboxylic acid **2**. [20b] Subsequent reaction of **2** with pyda under reflux condition in ethanol (95%) afforded **LH**$_2$ as a proton-transfer compound. The synthesis of **LH**$_2$ was also carried out in the solid state by grinding the two components together (in the presence or absence of triethylamine), reaction being indicated by a change in color of the resultant powder. Although the yield for both methods was almost the same (≅70%), the former was found to be more convenient and easier to scale-up. The melting point of **LH**$_2$ was sharp and different from the starting materials.

A search in the literature on the characterization of the proton-transfer compounds involving carboxylic acids and amines indicated that IR spectroscopy has been widely used as a diagnosticly useful tool for investigation of the nature of the interaction in such compounds.[25] The most definitive feature in the composite spectrum is the presence of strong asymmetric and symmetric carboxylate stretching frequencies at 1550−1610 and 1300−1420 cm^{-1}, respectively.[26] As reported in the Experimental Section, the first feature in the IR spectrum of **LH**$_2$ is the characteristic loss of the broad carboxyl O−H stretching frequency (2500−3300 cm^{-1}) together with the presence of asymmetric and symmetric carboxylate stretching frequencies at 1600 and 1380 cm^{-1}, respectively. Additional evidence for the formation of **LH**$_2$ can be achieved from the presence of a broad medium band between 1800−2000 cm^{-1}, confirming the presence of ammonium salt.

The NMR spectroscopic studies were conducted to further characterize the chemical structure of **LH**$_2$. A comparison between ^{1}H and ^{13}C NMR spectra of **LH**$_2$ and the corresponding dicarboxylic acid, recorded in DMSO-d_6, clearly indicated the presence of both 1,10-phenanthroline and pyridine rings in **LH**$_2$. From the selected ^{13}C NMR data of $[\text{pyda}\cdot H_2]^{2+}$, phendc·$H_2$, and **LH**$_2$ (Table 2), it is apparent that C(2) and C(9) (phen) shift greatly downfield ($\delta = 5.65$ ppm) upon deprotonation of phendc·H_2. Such a downfield shift for the directly attached carbons to the carboxylate anion group was previously observed for doubly deprotonated $[\text{pydc}]^{2-}$ too.[17] It was found that neither the carboxylate anions nor the directly attached carbons to the protonated amine sites were much affected by the proton-transfer process.

Table 2. Selected ^{13}C Data (ppm, DMSO-d_6) of $[\text{pyda}\cdot H_2]^{2+}$, phendc·$H_2$, and **LH**$_2$

C(*i*)[a]	$[\text{pyda}\cdot H_2]^{2+}$	[phendc·H_2]	**LH**$_2$
C(3,5) (py)	95.0[b]	−	95.0
C(4) (py)	144.8[b]	−	143.7
C(2,6) (py)	152.1[b]		151.7
C(2,9) (phen)	−	148.8	154.4
C=O (phen)	−	166.8	168.7

[a] The numbering system applied is the one normally used for pyridine and phenanthroline. [b] Taken from ref 17.

Table 3. UV/Vis Data (nm) of phendc·H_2, pyda, and **LH**$_2$

compd	λ_1	λ_2	λ_3
phendc·H2	234.4	285.6	
pyda	241.9		331.0
LH$_2$	235.3	285.6	329.6

The results of ES-MS under two carrier conditions, a mixture of CH_3OH/NaCl and a mixture of 0.2% formic acid in CH_3OH/CH_3CN, showed two important peaks at *m/z* 110.0 and 269.2. These data confirm the existence of $[\text{pyda}\cdot H]^+$ and $[\text{phendc}\cdot H_3]^+$ fragments in **LH**$_2$ aggregate, in agreement with the results obtained from NMR. The application of the ES-MS technique on our previous proton-transfer compound prepared from dipicolinic acid and pyda showed a proper molecular ion peak.[17] However, in the present case, the appropriate ion peak corresponding to **LH**$_2$ was not observed under the condition applied. It should be noted that the carrier influences the pattern of the resulting spectrum.

Finally, the formation of 1:1 proton-transfer compound **LH**$_2$ in solution was further confirmed by UV/vis data (Table 3), which shows the characteristic bands of both phenanthroline and pyridine units.

Synthesis and Characterization of $[\text{pyda}\cdot H]_2[\text{Co(phendc)}_2]\cdot 10H_2O$. The reaction of **LH**$_2$ with 0.5 M equiv of $Co(CH_3COO)_2\cdot 4H_2O$ afforded a green solution from which dark green crystals were obtained. The crystals changed into green powder upon drying in air, due to the partial loss of water of crystallization. Elemental analysis of the powder compound confirmed the chemical formula $[\text{pyda}\cdot H]_2[\text{Co(phendc)}_2]\cdot 6H_2O$. One of the features of the IR data of the Co(II) complex is the separation between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ that has been often used to diagnose the coordination modes in the carboxylate ligands.[27] The separation for unidentate carboxylato groups is >200 cm^{-1}, whereas it is <200 cm^{-1} in bidentate ones.[27,28] Thus, the separation of 257 cm^{-1} in the present Co(II) complex indicated a unidentate coordination mode for the coordinated carboxylate groups. The coordinated COO$^-$ stretching band appeared at 1590−1650 cm^{-1} and lattice waters at 3200−

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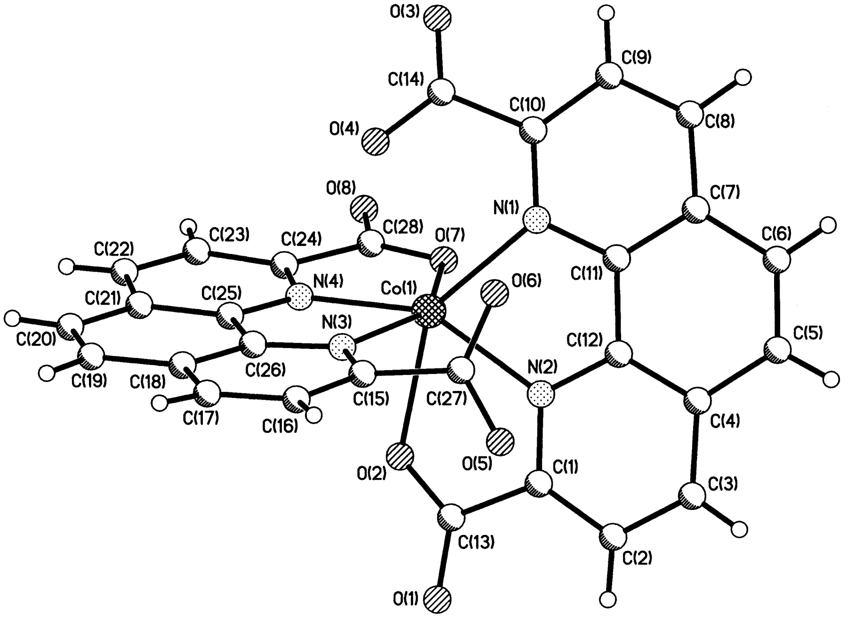

Figure 1. The molecular structure of the $[Co(phendc)_2]^2$ complex.

3550 cm^{-1} (asymmetric and symmetric OH stretching) and 1600−1630 cm^{-1} (HOH bending). Another feature of the IR spectrum was the presence of a band at 283 cm^{-1} which is within the range of 180−290 cm^{-1} considered for ν(Co−N).[28]

X-ray Crystal Structure of Co(II) Complex. Among a number of proton-transfer compounds obtained from carboxylic acids and amino derivatives of nitrogen heteroaromatics, few X−ray crystal structures have been reported to date.[12,17] Our efforts to get suitable single crystal of **LH**$_2$, however, failed. Therefore, to reconfirm that **LH**$_2$ exists as a proton-transfer compound, single-crystal structure determination of the resulting Co(II) complex was undertaken. Moreover, we were interested in observing the influence of the counterion $[pyda{\cdot}H_2]^{2+}$ in the complexation as well as the ligation and stereochemistry of the complex.

The molecular structure of the complex with atom numbering scheme and the crystal packing diagram are presented in Figures 1 and 2, respectively. The selected bond distances and angles and intermolecular hydrogen-bond distances are listed in Tables 4 and 5, respectively. An important feature of the crystal structure is the presence of $[pyda{\cdot}H]^+$ ion and complexation of 1,10-phenanthrolinedicarboxylic acid in its doubly deprotonated form as a tridentate ligand. The lattice consists of $[phendc]^{2-}$, $[pyda{\cdot}H]^+$, and water molecules. It is clear the presense of $[pyda{\cdot}H_2]^{2+}$ in the **LH**$_2$ ligand facilitates the formation of an anionic complex. The metal center is hexacoordinated by four nitrogen atoms (N(1)−N(4)) of phenanthroline rings, and two oxygen atoms (O(2), O(7)) of carboxylato groups of $[phendc]^{2-}$ tridentate ligands. The metal to nitrogen distance varies from 2.0409(15) to 2.2674(15) Å. The two longer Co−N distances (Table 4) are concerned with those (N(1), N(3)) that are closer to the free uncoordinated carboxylate groups. The two Co−O bond lengths are not the same (2.2021(14) and 2.3241(13) Å). The N(1)−Co−O(2) and O(7)−Co−N(3) bond angles are 143.11(5) and 151.24(5)°, respectively, providing a distorted tetrahedral arrangement around the cobalt center in CoN_2O_2 (N(1), N(3)) segment. The two $[phendc]^{2-}$ ligands are almost perpendicular to each other (Table 4), and both free uncoordinated carboxylates are linked bidentically to $[pyda{\cdot}H]^+$ cations (Figure 2) via strong hydrogen bonding interactions (Table 5). The water molecules are also hydrogen-bonded to both free and coordinated carboxylates as well as to the cations and play a crucial role in the crystal structure framework. This might be the reason the partial loss of lattice waters, upon drying

Table 4. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for $[pyda{\cdot}H]_2[Co(phendc)_2]{\cdot}10H_2O$

Co−N(1)	2.1580(15)	Co−O(7)	2.2021(14)
Co−N(3)	2.2674(15)	O(1)−C(13)	1.243(2)
Co−N(2)	2.1135(15)	O(2)−C(13)	1.262(2)
Co−N(4)	2.0409(15)	O(7)−C(28)	1.256(2)
Co−O(2)	2.3241(13)	O(8)−C(28)	1.258(2)
N(2)−Co−N(1)	75.16(5)	N(4)−Co−N(1)	134.84(6)
N(4)−Co−N(3)	76.31(6)	N(2)−Co−N(3)	97.17(6)
N(2)−Co−O(2)	70.29(5)	N(1)−Co−N(3)	111.60(5)
N(4)−Co−O(7)	75.15(5)	N(4)−Co−N(2)	149.81(6)
N(1)−Co−O(7)	86.56(5)	O(7)−Co−O(2)	92.80(5)
N(3)−Co−O(2)	85.56(5)	N(1)−Co−O(2)	143.11(5)
N(2)−Co−O(7)	109.30(6)	O(7)−Co−N(3)	151.24(5)
N(4)−Co−O(2)	79.76(5)		
N(1)−Co−N(3)−C(26)	136.10(11)	N(1)−C(10)−C(14)−O(3)	−154.70(17)
N(2)−Co−N(4)−C(25)	78.68(17)	N(3)−C(15)−C(27)−O(6)	65.1(2)
N(4)−Co−N(1)−C(10)	−1.97(17)	N(2)−C(1)−C(13)−O(2)	7.2(2)
N(3)−Co−N(1)−C(10)	−93.96(14)	N(4)−C(24)−C(28)−O(7)	2.1(2)
N(4)−Co−N(2)−C(1)	−3.3(2)	C(16)−C(15)−C(27)−O(5)	68.2(2)
N(3)−Co−N(2)−C(1)	71.72(14)	C(16)−C(15)−C(27)−O(6)	−110.6(2)
N(1)−Co−N(3)−C(15)	48.38(16)	C(2)−C(1)−C(13)−O(2)	−168.82(17)
N(1)−Co−N(4)−C(24)	68.21(15)	C(23)−C(24)−C(28)−O(7)	179.81(17)
O(7)−Co−N(2)−C(1)	−96.88(13)	C(9)−C(10)−C(14)−O(3)	25.7(3)
O(2)−Co−N(4)−C(24)	−96.92(13)	C(9)−C(10)−C(14)−O(4)	−155.11(17)

Table 5. Selected Hydrogen Bond Distances (Å)

N(5K)−H(5B)···O(3)	2.17	O(2S)H(2′)···O(1)	1.88
N(4K)−H(4N)···O(4)	1.78	O(4S)−H(4″)···O2	1.91
N(2K)−H(2B)···O(5)	1.96	O(10S)−H(10″)···O(5)	1.94
N(1K)−H(1N)···O(6)	1.86		

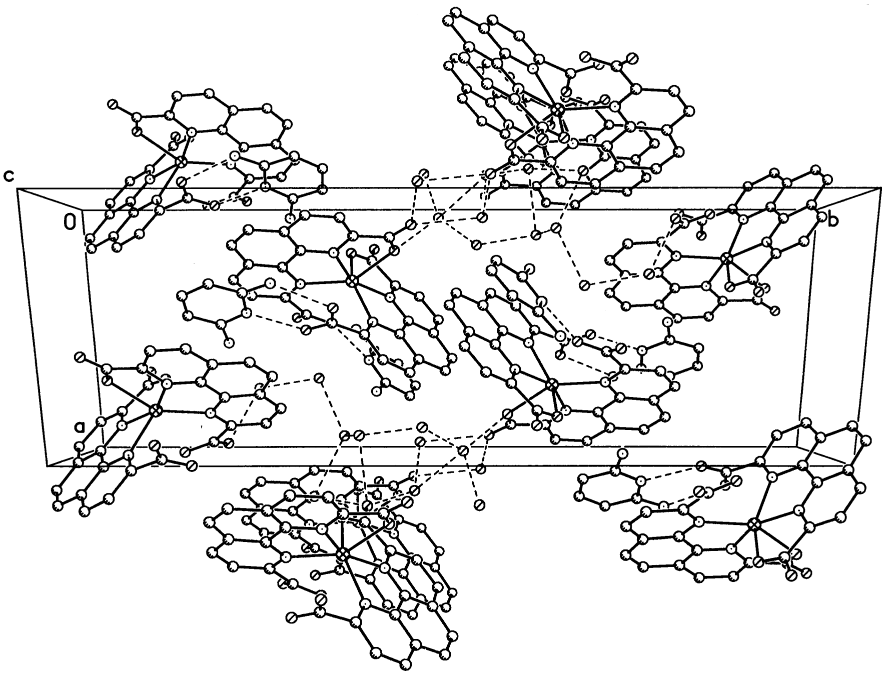

Figure 2. Unit cell packing diagram of $[pyda{\cdot}H]_2[Co(phendc)_2]{\cdot}10H_2O$.

in air, resulting in its subsequent change into a powderish compound. The $[pyda{\cdot}H]^+$ cations are also potentially susceptible to having hydrogen-bonding interactions. Therefore, because of the existence of both ion-pairing and extensive H-bonding, this complex should have a high lattice energy.

It is interesting to note that the protonated site in the cationic counterion in the Co(II) complex is the pyridine nitrogen. The same behavior has also been observed in the complexation of the previously reported proton-transfer compound,[17] $[pyda{\cdot}H]_2{}^+[pydc]^{2-}$, with some cations.[18] Thus, an interesting issue in connection with proton transfer from carboxylic acids, as donor, to amines, as acceptor, is the protonated site. The literature survey shows that there are examples of single proton-transfer compounds resulting from amino nitrogen heteroaromatic compounds, in which the ring nitrogens are protonated, e.g. 2-aminopyrimidine with 2-nitrobenzoic acid,[13a] trinitrobenzoic acid,[29] salisylic acid,[30] and dihydroxybenzoic acid;[29] 3-amino-1,2,4-triazine with 4-nitrobenzoic acid,[29] dinitrobenzoic acid,[31] and $pydc{\cdot}H_2$;[32] 8-aminoquinoline with nitro-substituted benzoic acids;[12b] and 2-aminopyridine with 2,6-dihydroxybenzoic acid.[30a] The more closely related examples reported recently are single proton transfer from 2,4,6-trinitrobenzoic acid[12c] and 2-nitrobenzoic acid[12d] to pyda. The most relevant example is a very recently reported case,[17] $[pyda{\cdot}H]_2{}^+[pydc]^{2-}$, which can be synthesized from a double proton-transfer reaction between $pydc{\cdot}H_2$ and pyda. On the basis of the X-ray crystal structure of this self-assembled compound, it was found that the two protonated sites are two $-NH_2$ nitrogens. Interestingly, once this compound participates in the complexation reaction with metal ions, the double protonated cationic counterion $[pyda{\cdot}H_2]^{2+}$ is changed to single protonated $[pyda{\cdot}H]^+$ counterion with the protonated site being the pyridine nitrogen, similar to the examples mentioned for the single proton-transfer compounds. On the basis of the examples given for both single and double proton transfer to pyda, it is predicted that the two protonated sites in the case of $\mathbf{LH}_2$ are two $-NH_2$ nitrogens, as depicted in Scheme 1. The isolation of suitable single crystals of $\mathbf{LH}_2$ for X-ray has not been successful yet.

Solution Studies. To obtain some information about the protonation constants of the building blocks of the $\mathbf{LH}_2$, in preliminary experiments, the fully protonated forms of the diamine (pyda) and diacid ($phendc{\cdot}H_2$) were titrated with a standard NaOH solution in 50:50 ethanol−water solution. The resulting equilibrium potentiometric pH titration profiles are shown in Figure 3a,b, respectively. The protonation constants ($K_n^H = [H_mL]/[H_{(m-n)}L][H]$) were calculated by fitting the potentiometric pH data to the program BEST.[24] The results are listed in Table 6. The species distributions of the tested compounds pyda and phendc are shown in Figure 4. It is seen that both compounds exist solely in completely deprotonated form at $pH > 9$, while the three protonated forms of pyda and four protonated forms of $phendc{\cdot}H_2$ show their maximum amounts at about pH 7.2 and lower.

The cumulative stability constants, β_{pqr}, of H^+ complexes with pyda, phendc, and $\mathbf{LH}_2$ as well as the resulting Co^{2+} complex with $\mathbf{LH}_2$ are defined by eq 1 (charges are omitted for simplicity).

$$pM + qL + rH \overset{\beta_{pqr}}{\rightleftharpoons} M_pL_qH_r \qquad \beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$$

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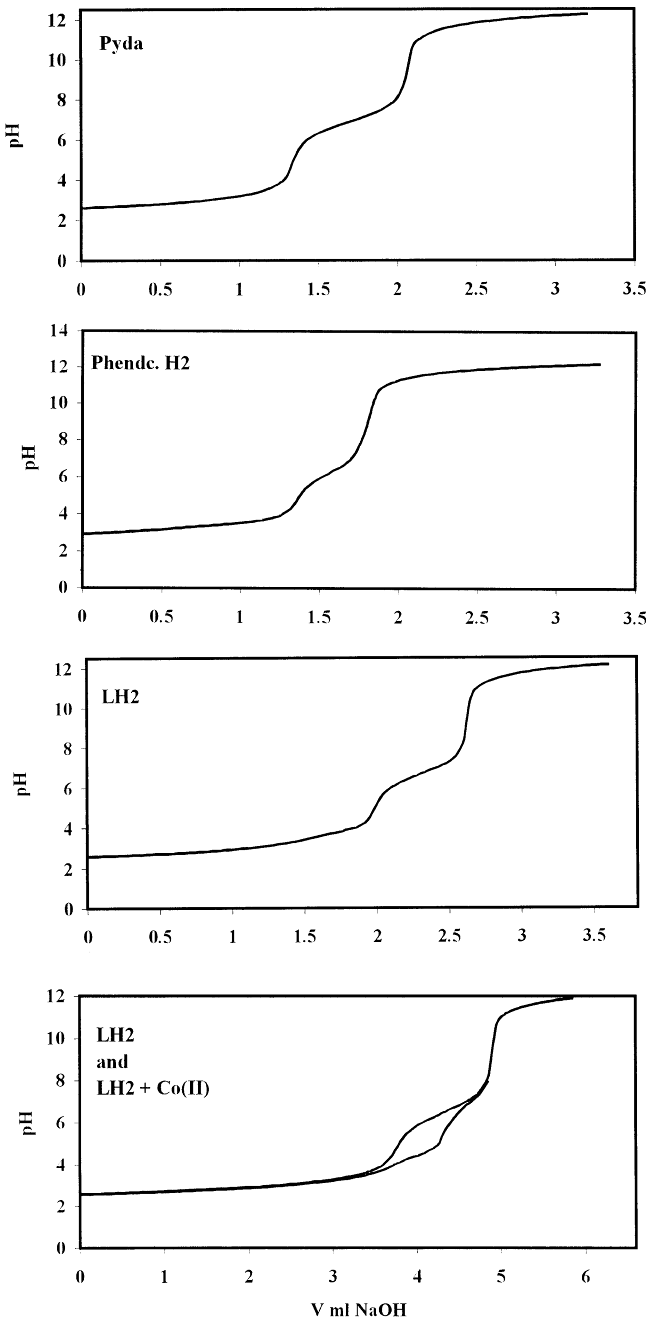

Figure 3. Potentiometric pH titration curves of four systems in 50:50 water/ethanol solutions: (a, top) 2.0 × 10^{-3} M pyda; (b, second from top) 8.0 × 10^{-3} M phendc·H_2; (c, third from top) 7.89 × 10^{-4} M $\mathbf{LH_2}$; (d, bottom) 7.35 × 10^{-4} M $\mathbf{LH_2}$ in the absence and presence of 3.45 × 10^{-4} M Co^{2+} at 25 °C and ionic strength of 0.1 M ($NaNO_3$).

Table 6. Stoichiometry (*p.q.r*), Notations, Logarithm of Cumulative Stability Constants[a] (log β), Logarithm of Protonation Constants (log *K*) for the Four H^+-pyda, H^+-phendc, H^+-$\mathbf{LH_2}$, and H^+-Co^{2+}-$\mathbf{LH_2}$ Systems at 25 °C and Ionic Strength of 0.1 M ($NaNO_3$)

ligand (L)	cation	(*p.q.r*)	notation	log β	log *K*	max (%)	at pH
pyda	H^+	(0.1.1)	$[pyda{\cdot}H]^+$	7.22	7.22	98.6	5.0
		(0.1.2)	$[pyda{\cdot}H_2]^{2+}$	10.12	2.90	54.0	2.5
		(0.1.3)	$[pyda{\cdot}H_3]^{3+}$	12.28	2.16	55.9	2.0
phendc		(0.1.1)	$[phendc{\cdot}H]^-$	6.96	6.96	96.6	5.2
		(0.1.2)	$[phendc{\cdot}H_2]^o$	10.38	3.42	36.2	3.4
		(0.1.3)	$[phendc{\cdot}H_3]^+$	13.64	3.26	49.5	2.8
		(0.1.4)	$[phendc{\cdot}H_4]^{2+}$	16.20	2.56	77.6	2.0
L		(0.1.1)	$[\mathbf{L}{\cdot}H]^-$	7.91	7.91	71.9	7.2
		(0.1.2)	$[\mathbf{L}{\cdot}H_2]^o$	14.40	6.49	85.9	5.4
		(0.1.3)	$[\mathbf{L}{\cdot}H_3]^+$	18.72	4.32	67.8	3.7
		(0.1.4)	$[\mathbf{L}{\cdot}H_4]^{2+}$	21.76	3.04	42.7	2.9
		(0.1.5)	$[\mathbf{L}{\cdot}H_5]^{3+}$	24.20	2.94	21.5	2.6
		(0.1.6)	$[\mathbf{L}{\cdot}H_6]^{4+}$	26.82	2.62	32.7	2.3
		(0.1.7)	$[\mathbf{L}{\cdot}H_7]^{5+}$	29.11	2.37	63.6	2.0
	Co^{2+}	(1.1.0)	$[Co\mathbf{L}]^o$	11.37	11.37	37.6	6.8
		(1.1.1)	$[Co\mathbf{L}{\cdot}H]^+$	16.69	5.32	79.4	3.9
		(1.1.2)	$[Co\mathbf{L}{\cdot}H_2]^{2+}$	19.59	2.90	31.2	3.0
		(1.2.0)	$[Co\mathbf{L}_2]^{2-}$	15.76	6.17	14.6	7.0
		(1.2.1)	$[Co\mathbf{L}_2{\cdot}H]^-$	23.01	7.25	26.0	7.0
		(1.2.2)	$[Co\mathbf{L}_2{\cdot}H_2]^o$	29.76	6.75	57.6	5.7

[a] Uncertainties in the cumulative stability constants estimated as ±0.5 of the last significant digit.

where L is the ligand, M is the metal ion, H is the proton, and *p*, *q*, and *r* are the respective stoichiometric coefficients. Since the ligand and complex activity coefficients are unknown, the β_{pqr} values are defined in terms of concentrations. The errors are minimized by use of a high constant ionic strength (0.1 M $NaNO_3$) and low ligand concentration.

A literature survey on the pK_a values of phendc·H_2 showed no experimental data. The four log protonation constants (6.96, 3.42, 3.26, and 2.56) for the phendc system are presented in Table 6. The first two values correspond to the two phendc nitrogens, and the last two represent the protonation of carboxylic functions. The obtained values are comparable to the corresponding values reported for 2,6-pyridinedicarboxylic acid by Crans et al.[33] The three log protonation constants in 2,6-pyridinedicarboxylic acid are 4.49, 2.03, and 0.5. The former being the value for pyridine nitrogen. Two other sources have reported close values (4.63[34] and 4.76[35]) for the protonation of pyridine nitrogen of this diacid. According to a recent publication,[36] the three pK_a's for 4-(4-aminophenylethynyl)pyridine-2,6-dicarboxylic acid are as 3.54, 2.58, and 1.01. It is noted that the ΔK of 0.7 corresponding to two −COOH functions of phendc·H_2 is very close to the required value 0.6 that has been considered for statistical separation for two noninteracting carboxylic groups belonging to the same molecule. This difference in 2,6-pyridinedicarboxylic acid, for instance, is 1.57 as reported by Bünzli et al.[36]

As it is seen from Table 6, three protonation constants were obtained for the pyda system. The log $K = 7.22$ value corresponding to the pyridine nitrogen is quite far from two other values, 2.90 and 2.16, that are attributed to two $-NH_2$ nitrogens. As expected, the pK_a value of pyda pyridine nitrogen is greater than the reported 6.82 and 5.25 values[37] for 2-aminopyridine and pyridine nitrogens, respectively. From a comparison between the log *K* values of the two −COOH functional groups of phendc·H_2 and the two first higher values of the pyda system, it can be predicted that proton transfer from phendc·H_2 to pyda can take place in solution so that a double-proton-transfer compound $\mathbf{LH_2}$ is

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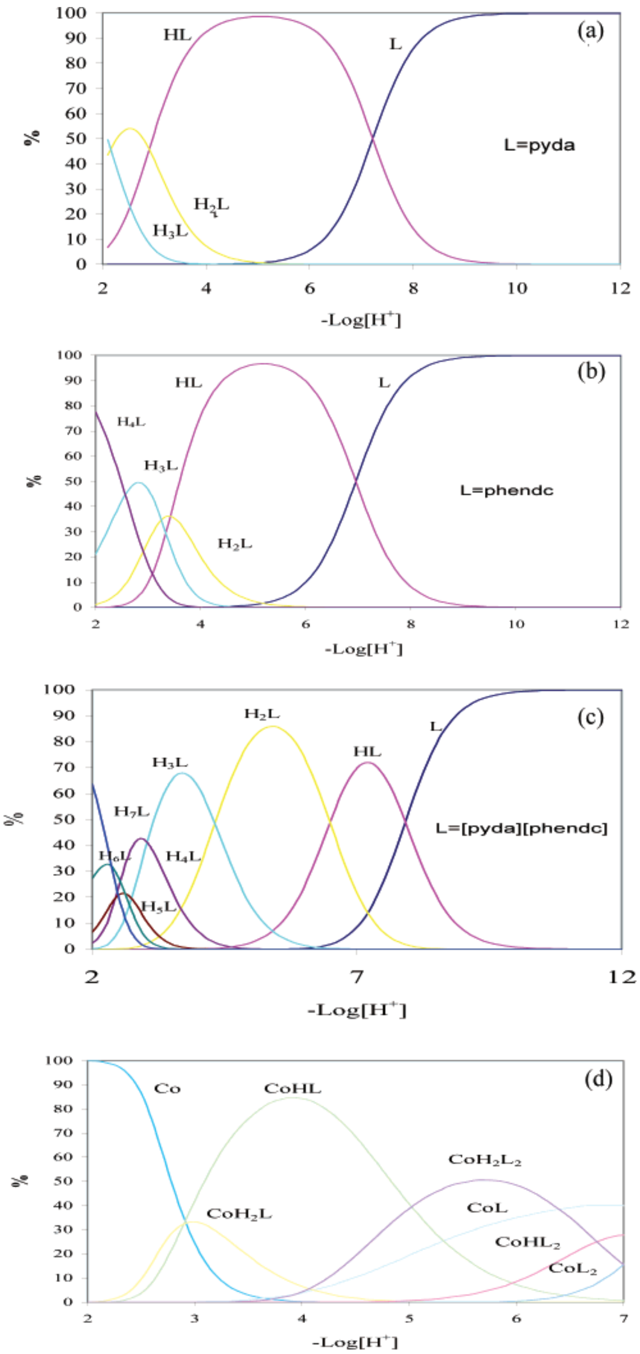

Figure 4. Distribution diagrams for pyda, phendc$\cdot H_2$, and $\mathbf{LH_2}$ in the absence and presence of Co^{2+} systems (from top to bottom).

produced, although the Δ log K^H value of the proton donor and proton acceptor in the present case has not reached to the required 3.75 value suggested in the literature.[38] Interestingly, upon complexation of 2 mol of $\mathbf{LH_2}$ with $Co(CH_3COO)_2$, the two initial doubly protonated $[pyda\cdot H_2]^{2+}$ counterions of $\mathbf{LH_2}$ are changed to two single-protonated $[pyda\cdot H]^+$, the $[pyda\cdot H]_2[Co(phendc)_2]$ complex is formed, and 2 mol of acetic acid are generated in solution.

The equilibrium potentiometric pH titration profiles of $\mathbf{LH_2}$ in the absence (panel c) and presence of Co^{2+} ion in a 1:2 (Co^{2+}:$\mathbf{LH_2}$) ratio are also included in Figure 3. As it is immediately obvious, the potentiometric titration curve of the $\mathbf{LH_2}$ system is depressed significantly in the presence of Co^{2+} ion, emphasizing the occurrence of some metal ion complexation with $\mathbf{LH_2}$ in solution. The resulting protonation constants of $\mathbf{LH_2}$ system, as calculated by the program BEST,[24] are also presented in Table 6. A comparison between the protonation constants of the $\mathbf{LH_2}$ system and those of the two components, pyda and phendc$\cdot H_2$, from which it is formed, indicates some expected measurable differences due to the transfer of two protons of the diacid to the diamine molecules, in the process of proton-transfer compound formation in solution. The occurrence of such proton donor−acceptor interaction would presumably cause an increase in the protonation constants of phendc$\cdot H_2$ (especially the K_1^H and K_2^H values), while a decrease in those of the pyda. It is interesting to note that the species distribution of the $\mathbf{LH_2}$ system shown in Figure 4c is also indicative of some changes in the extent and position of protonated species, in comparison with those of the free diamine and diacid (Figure 3a,b). The abbreviations L^{2-}, LH^-, LH_3^+, and $L_2H_2^{2-}$ in Figure 3c,d denote the $\{[pyda][pydc]\}^{2-}$, $\{[pyda\cdot H][phendc]\}^-$, $\{[pyda\cdot H_2][phendc\cdot H]\}^+$, and $\{[pyda\cdot H]_2[phendc]_2\}^{2-}$ species, respectively.

The potentiometric pH titration curve of $\mathbf{LH_2}$ in the presence of Co^{2+} ion was fitted to the program BEST, to calculate the cumulative stability constants of the likely complexed species in solution. The results are also included in Table 6, and the species distribution diagram of $\mathbf{LH_2}$ in the presence of Co^{2+} ion is shown in Figure 4d. As it is seen, among different 1:1 complexes, CoLH species with an extent of about 80% at a range of about pH 3.6−4.2 forms the most abundant species in solution, while the maximum amounts of CoL (at pH 7.0) and $CoLH_2$ (at pH 3.0) are about 38 and 31%, respectively. On the other hand, a CoL_2H_2 complex is formed to an extent of about 57% in a range of about pH 5.2−6.2, while the amount of CoL_2H and, especially, CoL_2 species even at about pH 7.0 is much lower than that of the CoL_2H_2 complex. Interestingly, our previous reports[18d,e] on the solution complexation studies of Co(II) and Cu(II) with the self-assembled system $[pyda\cdot H_2][pydc]$ ($pydc\cdot H_2$ = 2,6-pyridinedicarboxylic acid), indicated that the complexes $[(pyda\cdot H)]_2[Co(pydc)_2]$ and $[(pyda\cdot H)]_2[Cu(pydc)_2]$ are formed to an extent of about 41 and 44% in ranges of about pH 4.0−4.5 and pH 3.5−5.5, respectively. The X-ray crystal structures obtained for the isolated Co(II) and Cu(II) complexes in those cases were exactly similar to the mentioned predominate solution structures. Thus, the previous and the present solution studies strongly support the predominance of the formation of $[(pyda\cdot H)]_2[Co(pydc)_2]$ and $[pyda\cdot H]_2[Co(phendc)_2]$ species in ranges of about pH 4.0−4.5 and pH 5.2−6.2, respectively, with a stoichiometry similar to that of the isolated crystalline complexes.

Conclusion

The present work has demonstrated that phendc$\cdot H_2$ and pyda are appropriate proton donor and proton acceptor in the preparation of the proton−transfer compound $\mathbf{LH_2}$. This has been concluded from both the characterization of the

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isolated resulting compound and the potentiometric solution studies. The protonation constants of the **LH**$_2$ are different from the primary components, pyda and phendc•H_2, from which **LH**$_2$ was obtained. This well-designed novel proton-transfer compound provides a suitable route for preparing the first structurally characterized anionic metal−organic coordination compound [pyda•H]$_2$[Co(phendc)$_2$]•10H_2O. The potentiometric pH titration data clearly indicate that among different possible 1:1 complex species in solution, CoL_2H_2 species is the major one in a range of about pH 5.2−6.2. This is strongly in support of that of the isolated crystalline complex. The anionic Co(II) complex thus obtained involves cationic counterions that play an important role in construction of extensive H-bondings among [phendc]$^{2-}$, [pyda•H]$^+$, and lattice H_2O molecules. Some useful properties of this complex such as water solubility and susceptibility to have extensive H-bonding interactions as well as possessing the 1,10-phenanthroline moiety, are expected to provide logical biological activities for the resulting complex. The in vitro biological activities of this complex are under investigation.

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Supporting Information Available: Tables giving crystal data and structure refinement, all atomic coordinates, bond lengths and angles, anisotropic thermal parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles, and an X−ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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