

## Synthesis, X-ray Crystal Structure and Solution Studies of Cu(II) Complexes of a Pyridine Containing Self-Assembling System

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The complexation of a novel pyridine containing self-assembling system **LH**<sub>2</sub>, ([pyda·H<sub>2</sub>] [pydc] (pyda = 2,6-pyridinediamine and pydc·H<sub>2</sub> = 2,6-pyridinedicarboxylic acid), with copper(II) acetate leads to the formation of an anionic self-assemble coordination compound, [(pyda·H)<sub>2</sub>][Cu(pydc)<sub>2</sub>]·H<sub>2</sub>O. The crystal system is monoclinic with a space group *P*2<sub>1</sub>/*n* and contains four molecules per unit cell. The unit cell dimensions are: *a* = 8.2567(19) Å, *b* = 13.097(31) Å, *c* = 23.384(6) Å and β = 94.685(5)°. The four carboxylate groups of two dianions are oriented in a flattened tetrahedral arrangement and the two dianionic units are almost perpendicular to each other. The axial N–Cu–N angle shows 2.65° deviation from linearity. The complexation reactions 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 concentration of individual complex species as a function of pH. The results revealed that, at pH = 4–5, the major complex species in solution is [(pyda·H)<sub>2</sub>][Cu(pydc)<sub>2</sub>].

**Key words:** self-assembling system, crystal structure, Cu(II) complex, potentiometric pH titrations

Chemists have been interested in preparing self-assembling systems in recent years [1]. In connections with such systems we synthesized a novel system containing pyridine unit, **LH**<sub>2</sub>, [pyda·H<sub>2</sub>][pydc], which arises from both ion pairing and hydrogen bonding simultaneously [2]. A recently known example of such systems is that reported by Schmuck for self-association of 5-(guanidine carboxyl)-1H-pyrrol-2-carboxylate in DMSO [3]. Our goal was to generate a self-assembling coordination compound by using a self-assembling system ligand.

In a very recent publication [4], some coordination complexes that self assemble in a two-dimensional phase has been reported. Accordingly, we were interested in investigating the influence of the counter ion [pyda·H<sub>2</sub>]<sup>2+</sup> in the production of self-assembling coordination compounds. We have succeeded, however, to make differ-

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ent mononuclear, binuclear and polymer complexes from  $\text{LH}_2$ . Some of these complexes possess  $[\text{pyda}\cdot\text{H}]^+$  as a counter ion.

In this paper we wish to report the results of the complexation of self-assembling ligand  $\text{LH}_2$  with Cu(II) in solution and its X-ray crystal structure data.

## EXPERIMENTAL

**Reagents:** 2,6-Pyridinediamine (98%) was purchased from Aldrich and 2,6-pyridinedicarboxylic acid (98%), triethylamine (99%), tetrahydrofuran (99.7%) were purchased from Merck. Potassium hydroxide, potassium nitrate, potassium hydrogen phthalate and copper(II) acetate monohydrate (>99%) were of analytical grade from Merck. Doubly distilled deionized water was used throughout. The synthesis of  $\text{LH}_2$  was performed using a previously reported procedure [2].

**Apparatus:** The IR spectra were recorded on a Perkin-Elmer 343 and 1720x spectrophotometer using KBr discs. Melting points were determined with a Buchi 520 and were not corrected. Elemental analyses were performed with a Perkin-Elmer 240 apparatus. A Pye-Unicam Spa Philips atomic absorption was used to determine the percentage of  $\text{Cu}^{2+}$  in the complex. All pH measurements were carried out with a model 632 digital pH meter (Metrohm) equipped with a combined glass-calomel electrode.

**Synthesis of  $[(\text{pyda}\cdot\text{H})_2][\text{Cu}(\text{pydc})_2]\cdot\text{H}_2\text{O}$ :** To a solution of  $(\text{CH}_3\text{COO})_2\text{Cu}\cdot\text{H}_2\text{O}$  (0.100 g,  $0.5 \times 10^{-4}$  mol) in water (20 ml) was added a solution of ligand  $\text{LH}_2$  (0.276 g,  $1 \times 10^{-4}$  mol) in water (100 ml) and the resulting green solution was stirred for 15 min. After two weeks the crystals were collected, washed with fresh distilled water and dried. The pure green crystals,  $[(\text{pyda}\cdot\text{H})_2][\text{Cu}(\text{pydc})_2]\cdot\text{H}_2\text{O}$  in 68% yield, were obtained, decomposed at 278°C. Anal. Calcd. for  $\text{C}_{24}\text{H}_{24}\text{CuN}_8\text{O}_9$ : C 45.56%, H 3.79%, N 17.72%, Cu 10.05%. Found, C 45.48%, H 3.80%, N 17.69%, Cu 10.00%. IR (KBr,  $\text{cm}^{-1}$ ) 3460 (s), 3360 (s), 3200 (s), 1920 (w), 1700 (w), 1660 (s), 1630 (s), 1610 (m), 1565 (m), 1485 (s), 1420 (s), 1360 (s), 1320 (s), 1280 (m), 1190 (w), 1135 (w), 1080 (m), 1040 (w), 980 (m), 910 (m), 850 (w), 820 (w), 770 (s), 720 (s), 680 (m), 585 (w), 560 (w), 480 (w), 440 (w), 400 (w), 365 (w), 260 (w).

**Crystal structure determination:** Data were collected on a Bruker SMART diffractometer equipped with a molybdenum sealed tube and a graphite monochromator, at 110 K. The final cell parameters were determined using the SAINT<sup>+</sup> [5] software. It was not necessary to apply decay or absorption corrections to the data. The data were reduced to give the number of unique reflections.

The structure was solved by automatic direct methods using SHELXTL-PC [6]. The structure was refined by full-matrix least-square analysis on  $F^2$  with SHELXL. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were located from subsequent difference Fourier maps and refined with individual temperature factors to a final  $R$ -value of 0.0476.

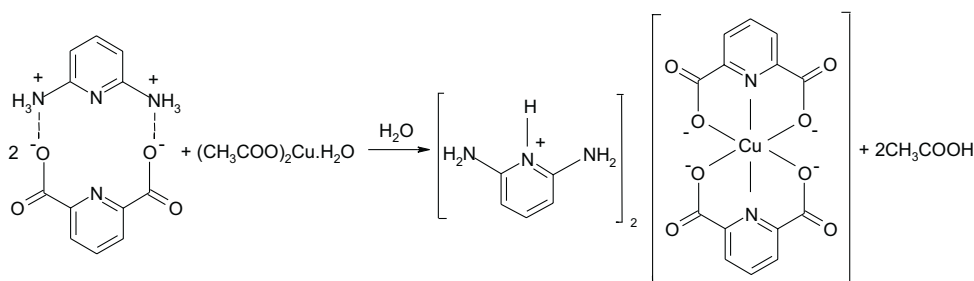
**pH-metric titrations:** The base used for potentiometric pH titrations was carbonate free potassium hydroxide, which was standardized against the primary standard oven-dried potassium hydrogen phthalate. A  $\text{CO}_2$ -free atmosphere for the base was ensured throughout.

The potentiometric apparatus used consisted of a 50-ml glass jacketed cell, a constant temperature bath (MLW thermostat,  $25.0 \pm 0.1^\circ\text{C}$ ), a combined glass electrode and a 10-ml capacity piston burette (Metrohm), for which the tip was sealed in the cap of the titration cell with a clamp and O-rings. Atmospheric  $\text{CO}_2$  was excluded from the titration cell with a purging stream of purified nitrogen gas. The electrodes were calibrated in the thermostated cell with standard acid-base to read pH directly. The value of  $K_w = [\text{H}^+][\text{OH}^-]$  used in the calculations was  $10^{-13.78}$  [7]. In all experiments, a  $1.0 \times 10^{-3}$  M solution of the ligand was used. The ionic strength was adjusted to 0.10 M with  $\text{KNO}_3$ . Before an experimental point (pH) was measured, sufficient time 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 [8].

## RESULTS AND DISCUSSION

**Synthesis and characterization of self-assembling Cu(II) complex:** The reaction between copper(II) acetate monohydrate and self-assembling system ligand, **LH<sub>2</sub>**, leads to the formation of a self-assembling coordination copper(II) compound (Scheme 1). The characterization of the resulting Cu(II) complex was performed using melting point, elemental analysis, IR, and X-ray crystallography. The melting point of Cu(II) complex was different from starting materials. The melting points were 235–237°C for the starting ligand **LH<sub>2</sub>** and 115°C for the salt (CH<sub>3</sub>COO)<sub>2</sub>Cu·H<sub>2</sub>O, while the complex decomposes at 278°C. The elemental analysis showed that the N, H, C, and Cu contents was completely different from the two known complexes [Cu(pydc·H)]·3H<sub>2</sub>O [9] and [Cu(pydc)(H<sub>2</sub>O)<sub>2</sub>] [10]. The elemental analysis data point on the formula C<sub>24</sub>H<sub>24</sub>N<sub>8</sub>O<sub>9</sub>Cu.



**Scheme 1.** The synthesis methods of [pyda·H]<sub>2</sub>[Cu(pydc)<sub>2</sub>]·H<sub>2</sub>O.

The next step to reach the chemical structures of the complex was the pattern of the IR spectra of **LH<sub>2</sub>** and the resulting Cu(II) complex. The carboxyl group bands at 1700 and 1340 cm<sup>-1</sup> in **LH<sub>2</sub>** shifted to 1630 and 1360 cm<sup>-1</sup>, respectively, suggesting that both carboxylate groups of the ligand [pydc]<sup>2-</sup> are coordinated to the Cu(II) ion. Of interest was also the NH and metal-heteroatoms bands. The NH bending band at 1580 cm<sup>-1</sup> in **LH<sub>2</sub>** shifted to a lower frequency of 1565 cm<sup>-1</sup> upon complexation. This could be due to the positive charge difference in [pyda·H<sub>2</sub>]<sup>2+</sup> and [pyda·H]<sup>+</sup> counter ions in **LH<sub>2</sub>** and Cu(II) complex. The difference in the protonation sites in these two cations may be the complementary reason. Out of a few new bands appeared in the IR spectrum of the Cu(II) complexes two are more important; *i.e.*, Cu–O and Cu–N metal-ligand bands that are positioned at 260, 365, 400, 440 and 480 cm<sup>-1</sup> [11,12].

**X-ray crystallographic structure of the Cu(II) complex:** To check the results obtained from the different techniques discussed, further studies were undertaken using X-ray crystallography. The numbering scheme and ORTEP diagram for the Cu(II) complex is shown in Fig. 1, and the unit cell packing diagram is illustrated in Fig. 2. The X-ray crystallographic data for the complex are presented in Table 1. Selected

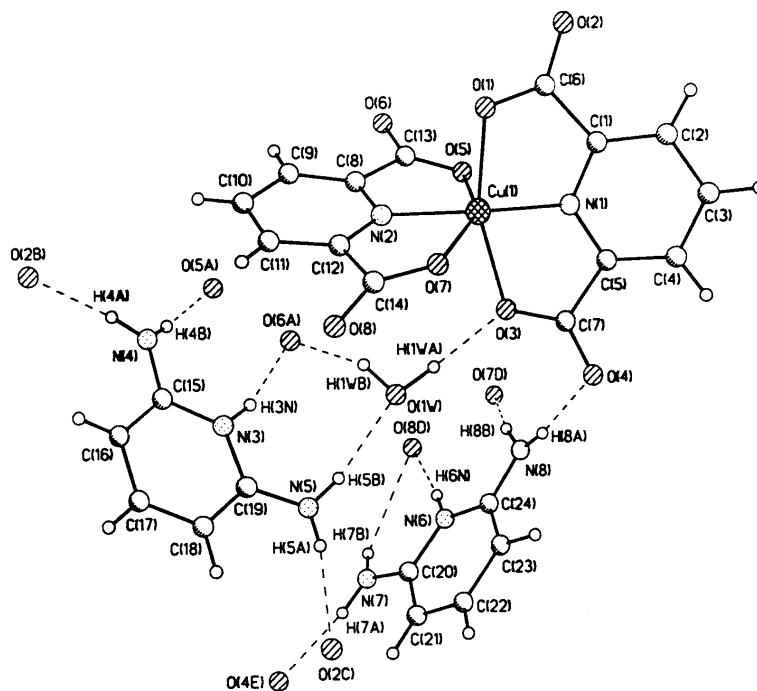


Figure 1. ORTEP plot for  $[\text{pyda-H}]_2[\text{Cu}(\text{pydc})_2] \cdot \text{H}_2\text{O}$ .

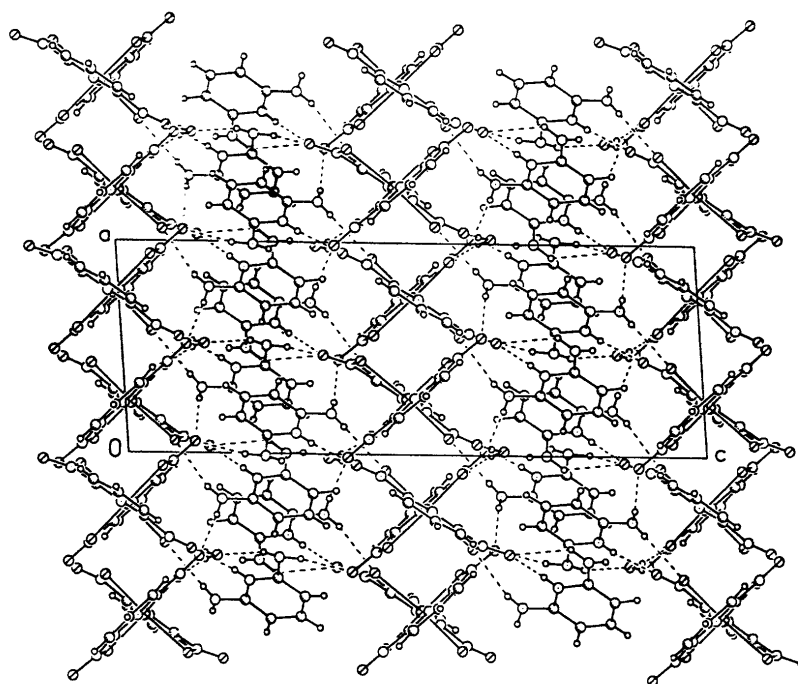


Figure 2. The unit cell packing diagram for  $[\text{pyda-H}]_2[\text{Cu}(\text{pydc})_2] \cdot \text{H}_2\text{O}$ .

bond lengths and angles, torsion angles and H-bonding data are presented in Tables 2–4. The ORTEP plot of the complex shows that the Cu(II) ions are located in the center of a distorted octahedral arrangement consisting of six donor atoms of the two tridentate  $[(\text{pydc})]^{2-}$ . The four carboxylate groups of the two dianionic ligands are oriented in a flattened tetrahedral arrangement around the Cu(II) atom. The N2–Cu–O3 and N2–Cu–O1 angles are  $103.1^\circ$  and  $97.52^\circ$ , respectively, and O3–Cu–N2–C8 and O1–Cu–N2–C12 torsion angles are  $-107.88^\circ$  and  $-99.77^\circ$ , respectively; thus, we can conclude that two dianionic  $[(\text{pydc})]^{2-}$  units are almost perpendicular to each other. The molecular structure consists of monomeric units  $[(\text{pyda}\cdot\text{H})]_2[\text{Cu}(\text{pydc})_2]\cdot\text{H}_2\text{O}$ , in which the two pydc units act as tridentate ligands. It is interesting to note that the protonated site in the cationic counter ion is the pyridine nitrogen atom, while the two protons in the ligand  $\text{LH}_2$  are located at the two  $-\text{NH}_2$  nitrogen positions.

**Table 1.** Crystal data and structure refinement for Cu(II) complex.

Empirical formula	$\text{C}_{24}\text{H}_{24}\text{N}_8\text{CuNiO}_9$
Formula weight	632.05
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 8.2567(19)$ Å $b = 13.097(3)$ Å $c = 23.384(6)$ Å $\beta = 94.685(5)^\circ$
Volume, $Z$	$2520.3(10)$ Å <sup>3</sup> , 4
Density (calculated)	1.666 g/cm <sup>3</sup>
Absorption coefficient	0.940 mm <sup>-1</sup>
$F(000)$	1300
Crystal size	$0.50 \times 0.3 \times 0.2$ mm <sup>3</sup>
Reflections collected	29580
Independent reflections	7307 [R(int) = 0.0359]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	7307/0/475
Goodness-of-fit on $F^2$	1.058
Final R indices	$R_1 = 0.0476$ , $wR_2 = 0.1229$
R indices (all data)	$R_1 = 0.0577$ , $wR_2 = 0.1310$
Largest diff., peak and hole	2.806 and $-0.761$ eÅ <sup>-3</sup>

**Table 2.** Selected bond lengths [Å] and angles [°] for Cu(II) complex.

Cu(1)–N(1)	1.9142(15)
Cu(1)–N(2)	1.9569(15)
Cu(1)–O(1)	2.0785(13)
Cu(1)–O(3)	2.0911(13)
Cu(1)–O(5)	2.3450(14)
Cu(1)–O(7)	2.4097(15)
N(1)–Cu(1)–N(2)	177.35(6)
N(1)–Cu(1)–O(1)	79.90(5)
N(2)–Cu(1)–O(1)	97.52(5)
N(1)–Cu(1)–O(3)	79.47(5)
N(2)–Cu(1)–O(3)	103.10(5)
O(1)–Cu(1)–(3)	159.36(5)
N(1)–Cu(1)–(5)	104.25(5)
N(2)–Cu(1)–O(5)	76.24(5)
O(1)–Cu(1)–O(5)	89.18(5)
O(3)–Cu(1)–O(5)	96.32(5)
N(1)–Cu(1)–O(7)	103.62(5)
N(2)–Cu(1)–O(7)	75.99(5)
O(1)–Cu(1)–O(7)	97.21(5)
O(3)–Cu(1)–O(7)	87.21(5)
O(5)–Cu(1)–O(7)	152.09(4)

**Table 3.** Selected torsion angles [°] for Cu(II) complex.

O(3)–Cu(1)–N(2)–C(12)	97.54(13)
O(1)–Cu(1)–N(2)–C(8)	72.82(13)
O(5)–Cu(1)–N(1)–C(1)	84.55(13)
O(7)–Cu(1)–N(1)–C(5)	81.53(13)
O(5)–Cu(1)–N(1)–C(5)	–96.88(13)
O(7)–Cu(1)–N(1)–C(1)	–97.04(13)
O(1)–Cu(1)–N(2)–C(12)	–99.77(13)
O(3)–Cu(1)–N(2)–C(8)	–107.88(12)

There are two important features of this complex, one of which is the existence of strong intramolecular forces between the anionic and cationic units in the Cu(II) complex, consisting of both H-bonding and ion-pairing, that cause the self-assemble Cu(II) complex into layers (Fig. 2), the other one is the presence of Jahn-Teller effect. In the Cu(II) complex, the two pydc units have different behavior: one of them is coordinated to the metal at appreciably longer distances (Cu–O5 and Cu–O7 bond distances are 2.3450 Å and 2.4097 Å, respectively (mean = 2.377 Å), with respect to

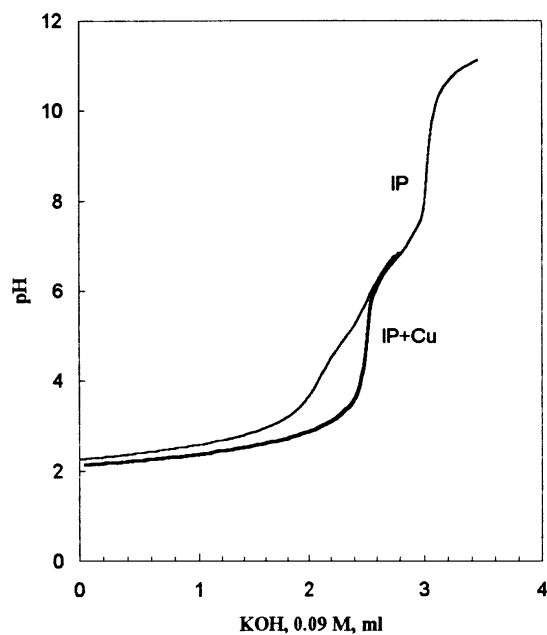
the other coordination atoms (Cu–O1, Cu–O3 bond distances are 2.0785 Å, 2.0911 Å, respectively (mean = 2.0848 Å). The Cu–N bond distances are 1.9142 Å and 1.9569 Å, (mean = 1.9355 Å). These distances are different from the corresponding bond distance values reported for imidazolium carboxylate Cu(II) complex [4]. For instance, Cu–N1, Cu–O2 and Cu–O3 in the imidazolium complex are 1.940 Å, 2.173 Å and 2.208 Å long, respectively. With respect to the axial N–Cu–N angle involving the nitrogen atoms on the two pyridyl ligands, a small deviation (2.65°) from linearity has been observed. This deviation is close to the deviation value reported for N–Cu–N in imidazolium carboxylate Cu(II) complex (1.5°). The data presented specify that these key bond distances and angles are affected by the nature of the cationic counterion. Therefore, the coordination around Cu(II) in [pyda·H]<sub>2</sub>[Cu(pydc)<sub>2</sub>·H<sub>2</sub>O] is bipyramidally distorted octahedron.

**Table 4.** Hydrogen bonds and angles for Cu(II) complex [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(3)–H(3N)...O(6A)#1	0.84(3)	1.96(3)	2.777(2)	165(2)
O(1W)–H(1WA)...O(3)	0.94(4)	1.97(4)	2.905(2)	171(3)
O(1W)–H(1WB)...O(6A)#1	0.98(4)	1.80(4)	2.736(2)	158(3)
N(4)–H(4A)...O(2B)#3	0.89(6)	2.05(5)	2.914(2)	164(2)
N(4)–H(4B)...O(5A)#1	0.72(3)	2.40(3)	3.109(2)	170(2)
N(5)–H(5A)...O(2C)#4	0.83(4)	2.36(3)	3.153(2)	160(2)
N(5)–H(5B)...O(1W)	0.90(3)	2.05(3)	2.912(2)	161(2)
N(6)–H(6N)...O(8D)#2	0.87(4)	1.76(4)	2.622(2)	173(2)
N(7)–H(7A)...O(4E)#5	0.90(3)	2.02(3)	2.900(2)	166(2)
N(7)–H(7B)...O(8D)#2	0.91(3)	2.55(3)	3.204(2)	130(2)
N(8)–H(8A)...O(4)	0.83(3)	2.10(3)	2.926(2)	171(2)
N(8)–H(8B0)...O(7D)#2	0.86(3)	2.42(3)	3.236(2)	159(2)

Symmetry transformations used to generate equivalent atoms: # 1  $-x + 1, -y + 1, -z$ ; # 2  $x + 1, y, z$ ; # 3  $-x, -y + 1, -z$ ; # 4  $x + 1/2, -y + 3/2, z + 1/2$ ; # 5  $-x + 3/2, y - 1/2, -z + 1/2$ .

**Solution studies:** The equilibrium potentiometric pH titration profiles of the self-assembling system **LH<sub>2</sub>** in the absence (A) and presence of Cu<sup>2+</sup> ion in a 1:2 Cu<sup>2+</sup>:(**LH<sub>2</sub>**)<sub>2</sub> ratio (B) are shown in Fig. 3. The protonation constants ( $K_n^H = [H_nL]/[H_{(n-1)}L][H]^n$ ) were calculated by fitting the potentiometric pH data to the program BEST [5]. The results are listed in Table 5, and the species distribution in the absence of metal ion is shown in Fig. 4. As is obvious from Fig. 4, the self-assembling system cannot exist at all at pH > 6.5 and pH < 1; at the high pH limits the partners exist as a neutral amine [pyda]<sup>0</sup> and a dicarboxylate anion [pydc]<sup>2-</sup>, while at the low pH limits they exist as a deprotonated amine [pyda·H<sub>2</sub>]<sup>2+</sup> and a neutral dicarboxylic acid [pydc·H<sub>2</sub>]<sup>0</sup>. However, maximum amount of the self-assembling system ([pyda·H<sub>2</sub>]<sup>2+</sup>[pydc<sup>2-</sup>], (**LH<sub>2</sub>**)) exists (at an about 90% level) at a pH range of about 3.2–3.6 in solution.



**Figure 3.** Potentiometric pH titration curves of  $\text{LH}_2$  in the absence (A) and presence of  $\text{Cu}^{2+}$  ion (B). Conditions:  $[\text{LH}_2] = 1.0 \times 10^{-3}$  M;  $[\text{Cu}^{2+}] = 5.0 \times 10^{-4}$  M;  $[\text{KNO}_3] = 0.1$  M.

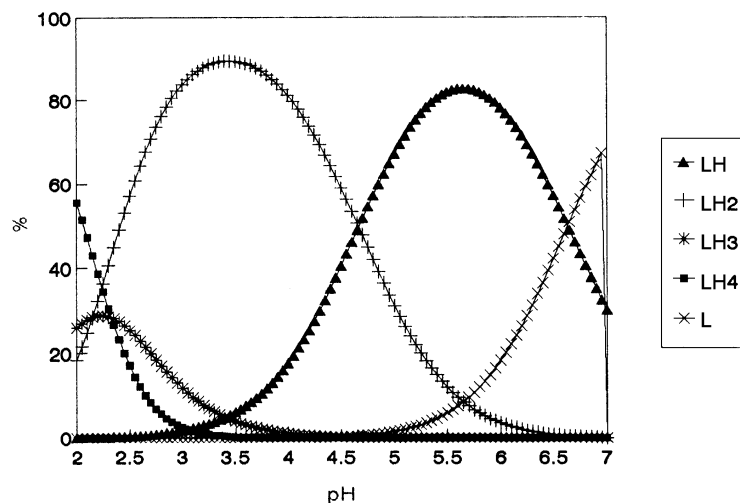
**Table 5.** Logarithm of cumulative stability constants of  $\text{H}^+$  and  $\text{Cu}^{2+}$  complexes with the self-assembling system  $\text{LH}_2$  at  $25^\circ\text{C}$  and ionic strength of 0.1 M.

Cation	Stoichiometry			Log $\beta^a$
	l	m	h	
$\text{H}^+$	1	0	1	6.63
	1	0	2	11.30
	1	0	3	13.45
	1	0	4	15.77
$\text{Cu}^{2+}$	1	1	0	7.38
	1	1	1	13.24
	2	1	0	12.23
	2	1	1	19.07
	2	1	2	25.76
	2	1	3	28.21

<sup>a</sup> Uncertainties in the cumulative stability constants estimated as  $\pm 0.5$  of the last significant digit.

As it is seen from Fig. 3, the potentiometric titration curve of  $\text{LH}_2$  system is depressed considerably in the presence of  $\text{Cu}^{2+}$  ion at the stoichiometries of the resulting





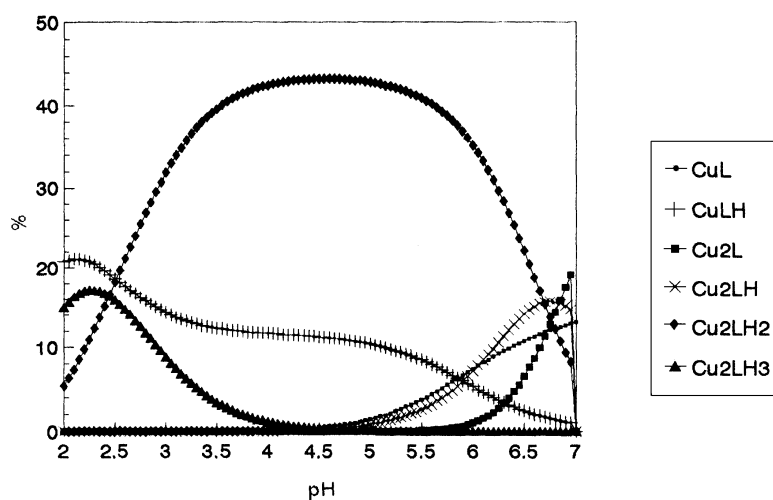
**Figure 4.** Distribution curves for the self-assembling system in the absence of  $\text{Cu}^{2+}$ : ( $\blacktriangle$ ) LH, (+) LH<sub>2</sub>, (\*) LH<sub>3</sub>, ( $\blacksquare$ ) LH<sub>4</sub>, ( $\times$ ) L.

complexes and the ability of metal ion to bind to the ligand components. The cumulative stability constants,  $\beta_{1mh}$  are defined by (1) (charges are omitted for simplicity)



where L is ligand, M is metal ion, H is proton, and 1, m and h are the respective stoichiometric coefficients. Since the ligand and complex activity coefficients are unknown, the  $\beta_{1mh}$  values are defined in terms of concentrations. The errors are minimized by use of a high constant ionic strength (0.1 M) and low ligand concentration ( $1.0 \times 10^{-3}$  M).

The potentiometric pH titration curve of **LH<sub>2</sub>** in the presence of  $\text{Cu}^{2+}$  ion was fitted to the program BEST, in order to calculate the cumulative stability constants of likely complexed species in solution. The results are also included in Table 5, and the species distribution diagram of **LH<sub>2</sub>** in the presence of  $\text{Cu}^{2+}$  ion is shown in Fig. 5. From Fig. 5, it is immediately obvious that negligible amounts of deprotonated  $\text{CuL}$  and  $\text{CuL}_2$  complexes are formed in solution, over entire pH range of 2.0 to 5.5, while the monoprotinated forms of these species (*i.e.*  $\text{CuLH}$  and  $\text{CuL}_2\text{H}$ ) show an extent of about 21% (at pH 2.5) and 18% (at pH 6.5), respectively. On the other hand, a  $\text{CuL}_2\text{H}_2$  complex (*i.e.*  $[(\text{pyda}\cdot\text{H})]_2[\text{Cu}(\text{pydc})_2]$ ) is formed to an extent of about 44% at a pH range of about 3.5–5.5 and decreases in concentration at higher and lower pH values in the expense of increased amount of  $\text{CuL}_2\text{H}$  and  $\text{CuLH}$ , respectively. Thus, the solution studies strongly support the predominance of the formation of a  $\text{CuL}_2\text{H}_2$  complexed species with a stoichiometry similar to that of the isolated crystalline complex.



**Figure 5.** Distribution curves for the 1:2  $\text{Cu}^{2+}$ :  $\text{LH}_2$  system: (■)  $\text{CuL}$ , (+)  $\text{CuLH}$ , (■)  $\text{CuL}_2$ , (×)  $\text{Cu}_2\text{LH}$ , (◆)  $\text{Cu}_2\text{LH}_2$ , (▲)  $\text{Cu}_2\text{LH}_3$ .

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**Supplementary data:** Crystallographic data for the structural analysis have been deposited in the Cambridge Crystallographic Data Centre (CCDC 176729). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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