A Proton Transfer and a Nickel(II) Compound Including Pyridine-2,6-dicarboxylate and Phenylhydrazinium Ions: Synthesis, Characterization, Crystal Structure and Solution Study

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The new compounds, $(phhyH)_2(pydc)$, **1** and $(phhyH)[Ni(pydc)(pydcH)].3H_2O$, **2**, phhy: phenylhydrazine, $pydcH_2$: pyridine-2,6-dicarboxylic acid, were synthesized and characterized by IR, ^1H NMR, ^{13}C NMR and UV spectroscopy. The structure of **2** was determined by X-ray crystallography. In the crystal structure, the metal ion was six coordinated by two tridentate $(pydc)^{2-}$ and $(pydcH)^-$ groups and each anionic complex unit, $[Ni(pydc)(pydcH)]^-$ was accompanied by one $(phhyH)^+$ as counter ion and two water molecules. In compound **2**, a large number of O-H···O, N-H···O and C-H···O hydrogen bonds were observed. These interactions as well as other noncovalent interactions such as ion pairing, C-O···π and π-π stacking play an important role in the formation and stabilization of the crystal lattice. In the solution study, the equilibrium constants for the binary pydc-phhy proton transfer system, the stoichiometry and stability of complexation of this system with Ni^{2+} ion in aqueous solution were investigated using potentiometric pH titration method. The stoichiometry of the most abundant species in the solution was compared to the crystalline cited metal ion complexes.

INTRODUCTION

With the rapid growth in supramolecular chemistry in recent years, a great deal of effort has been devoted to the design and assembly of supramolecular compounds, due to their potential applications in the ionophore chemistry, ion pair extraction chemistry, phase transfer catalysis chemistry and so on [1,2]. Moreover, the syntheses of various supramolecular compounds help to obtain new information

about intermolecular interactions, which is obviously crucial for the rational design and construction of new framework structures [3]. Recently, several types of forces, such as coordination bonding [4-9], hydrogen bonding [10-13], π-π stacking [14,15] and electrostatic interactions [16] have been well used in constructing extended supramolecular networks.

Our research group has been interested in the synthesis of proton transfer compounds as new supramolecular synthons for the one-pot preparation of self-assembled transition metal complex-organo-networks since 2000 [17]. The successful synthesis of these systems depends on the choice of the

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appropriate carboxylic acid, as proton donor, and amine, as proton acceptor, which interact with each other. Some examples of proton transfer self-assembled systems, prepared by employing this strategy, include organic heterocyclic amine carboxylates [18,19], oxalates [20] and squarates [21].

We have reported cases in which proton transfer from Pyridine-2,6-dicarboxylic acid (pydcH$_2$) to pyridine-2,6-diamine (pyda), guanidine (G), 1,10-phenanthroline (phen), creatinine (creat) and 2,4,6-triamino-1,3,5-triazine (tata) resulted in the formation of proton transfer compounds, (pydaH)(pydcH), (GH)$_2$(pydc), (phenH)$_2$(pydc), (creatH)(pydcH).H$_2$O and (tataH)$_2$(pydc) [17]. The importance of proton transfer compounds resides in their ability to act as complexing agents in polar solvents such as H$_2$O to form water soluble complexes. Several complexes of these systems have been synthesized and their X-ray crystal structures have been reported [17,22]. In continuation of our research projects, herein we report the synthesis, characterization and crystal structure determination of a nickel(II) compound obtained from a novel proton transfer compound containing phenylhydrazinium counter ion. This proton transfer compound is (phhyH)$_2$(pydc), (phhy = phenylhydrazine, pydcH$_2$ = pyridine-2,6-dicarboxylic acid). Noncovalent interactions in these compounds play an important role in the stabilization of the crystal lattice

EXPERIMENTAL

General Methods and Materials

Nickel(II) nitrate hexahydrate (99%), pyridine-2,6-dicarboxylic acid (97%) and phenylhydrazine (99%) were all purchased from Merck. The IR spectra were recorded on a Bruker vector 22 spectrophotometer (4000-400 cm^{-1}) using KBr disc. Melting points were determined applying a Branstead Electrothermal 9100 apparatus. Elemental analysis was performed with CHNS-O Elemental Analyzer Perkin-Elmer 2004(II) apparatus.

The X-ray data were obtained with a Bruker SMART Diffractometer. Single crystals of compound **2,** suitable for crystallography, were selected. Unit cell determination and the data of the compounds were collected on a Bruker SMART CCD area detector system [23] using Mo Kα radiation (λ = 0.71073 Å). The structures were solved and refined by full-

matrix least-squares techniques on F^2 using SHELX-97 (SHELXL program package) [24,25]. The absorption corrections type was multi-scan. The hydrogen atoms of NH$_2$ groups and water molecules were found in different Fourier syntheses. The H(C) atom positions were established.

All hydrogen atoms were refined in isotropic approximation in riding model with the U$_{iso}$(H) parameters equal to 1.2 U$_{eq}$(C$_i$), 1.2 U$_{eq}$(N$_i$) and 1.2 U$_{eq}$(O$_i$), where U(C$_i$), U(N$_i$), U(O$_i$) are respectively the equivalent thermal parameters of the carbon, nitrogen and oxygen atoms to which the corresponding H atoms are bonded. The refinement of F^2 was unlike all the reflections. The weighted R-factor wR and goodness of fit S are based on F^2, the conventional R-factors are based on F, with F set to zero for the negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc.*, and is not relevant to the choice of reflections for the refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on the whole data would be even larger.

Finally, A Model 794 Metrohm Basic Titrino was attached to an extension combined glass-calomel electrode mounted on an air-protected, sealed, thermostated jacketed cell maintained at 25.0 ± 0.1 °C by circulating water from a constant-temperature bath Fisherbrand model FBH604, LAUDA, Germany, equipped with a stirrer and a 10.000-ml-capacity Metrohm piston burette. The pH meter-electrode system was calibrated to read -log[H$^+$].

Synthesis and Spectroscopy of (phhyH)$_2$(pydc), 1

Starting with a solution of phenylhydrazine (0.196 g, 2 mmol) and pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) in THF, a white powder of (phhyH)$_2$(pydc), **1,** (phhy = phenylhydrazine, pydcH$_2$ = pyridine-2,6-dicarboxylic acid) was obtained, as shown in Scheme 1. M.p.: 196 °C. IR(KBr): 3730-3391 br,m, 3282 sh,m, 3098 m, 3080-2972 br,m, 1718 sh,s, 1626 s, 1592 sh,vs, 1570 s, 1542 s, 1501 s, 1437 sh,s, 1395 sh,s, 1337 sh,s, 1283 s, 1263 s, 1192 s, 1080 sh,s, 769 sh,s, 727 sh,s, 683 sh,s, 439 s, cm^{-1}. ^{1}H NMR (DMSO) = 3.69-4.67 (m, 1H, phhyH$^+$), 6.89-7.27 (m, 1H, phhyH$^+$), 6.913-7.27 (m, 2H, phhyH$^+$), 8.11-8.407 (s, 6H, pydc^{2-}) ppm. ^{13}C NMR (DMSO) = 115.48 (s, phhyH$^+$), 123.78 (m, phhyH$^+$), 127.71 (m, pydc^{2-}), 129.68 (s, phhyH$^+$), 145.36 (m, pydc^{2-}), 145.97 (m, phhyH$^+$), 164.90 (m, pydc^{2-}).
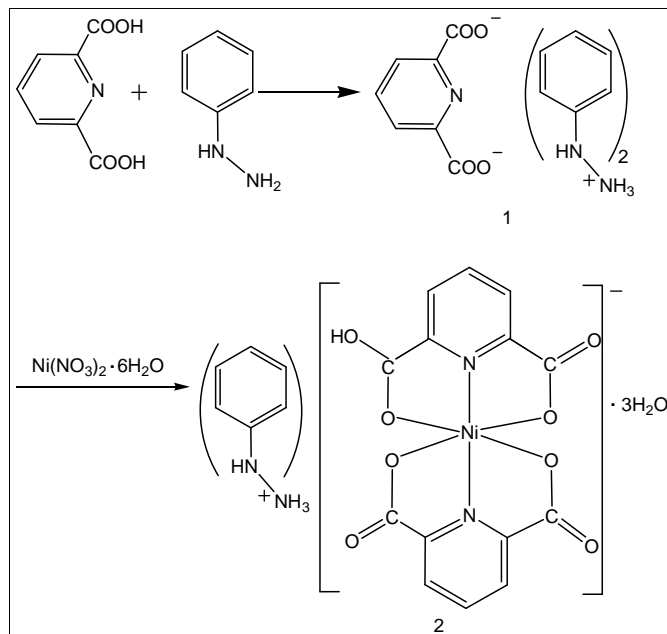
Scheme 1. Synthetic route to the title compounds

Synthesis and Spectroscopy of (phhyH)[Ni(pydc)(pydcH)]·3H$_2$O, 2

An aqueous solution of Ni(NO$_3$)$_2$.6H$_2$O (0.145 g, 0.5 mmol) was added to a stirring solution of **1** (0.363 g, 1 mmol) in water and stirred for half an hour, as shown in Scheme 1. On slow evaporation, green single crystals of **2** suitable for X-ray characterization were collected at room temperature after 3 weeks. M.p.: decomposed > 250 °C. Anal. Calcd. for C$_{20}$H$_{22}$N$_4$NiO$_{11}$, **2**: C, 43.40%; H, 3.98%; N, 10.12%; Found: C, 43.71%; H, 4.01%; N, 10.21%. IR(KBr): 3470-3310 br,m, 3284 s, 3099 s, 3070-2831 br,m, 1717 sh,s, 1624 s, 1590 sh,s, 1570 s, 1539 s, 1438 sh,s, 1394 sh,s, 1335 sh,s, 1283 s, 1240 s, 1190 s, 1079 sh,s, 769 sh,s, 727 sh,s, 682 sh,s, 437 s cm^{-1}. ^{1}H NMR (DMSO) = 3.74 (m, 1H, phhyH$^+$), 6.40 (m, 2H, phhyH$^+$), 6.87 (m, 1H, phhyH$^+$), 7.16-7.35 (m, 2H, phhyH$^+$), 8.20 (s, 6H, pydc^{2-}) ppm. ^{13}C NMR (DMSO) = 114.39 (s, phhyH$^+$), 121.91 (m, phhyH$^+$), 128.00 (m, pydc^{2-}), 129.38 (s, phhyH$^+$), 139.72 (m, pydc^{2-}), 145.49 (m, pydc^{2-}), 148.57 (m, phhyH$^+$), 165.94 (m, pydc^{2-}) ppm.

Solution Study Procedure

The details are well described in references [31-34]. The concentration of phhy and pydc was 2.5×10^{-3} M, for the potentiometric pH titrations of pydc, phhy and pydc-phhy, in the absence and presence of 1.25×10^{-3} metal ion. A standard carbonate-free NaOH solution (0.09623) was used in all titrations. The ionic strength was adjusted to 0.1 M with NaNO$_3$. Before an experimental point (pH) was measured, sufficient time was allowed for the establishment of equilibrium. Ligands' protonation constants and stability constants of proton transfer and their metal complexes were evaluated using the BEST program [35] and the corresponding distribution diagrams were depicted using Hyss2009 as a new version of Hyss2006 program [36]. The value of K$_w$ = [H$^+$][OH$^-$] was used in the calculations according to our previous works [31-33].

RESULTS AND DISCUSSION

Characterization of (phhyH)$_2$(pydc), 1

IR spectroscopy of compound **1** shows a strong, broad and branched peak at 3730-2972 cm^{-1} attributed to the aromatic C-Hs of phenyl and pyridine rings, as well as NH stretching vibrations which are well broadened and are seen in this range. Other strong peaks in 1395 and 1626 cm^{-1} are related to the resonance of (COO)$^-$. In fact, ν(C-O) and ν(C=O) bands are transformed into the symmetric and asymmetric stretching vibrations of the carboxylate anion [26]. In 1592 cm^{-1}, there is a very strong and sharp peak for scissoring the N-H of (phhyH)$^+$ ion, which is seen for neutral phenylhydrazine in 1600-1500 cm^{-1}. Sharp and relatively strong band in 1080 cm^{-1} is attributed to stretching C-N vibration. These bands are also present in the spectrum of phenylhydrazine in 1073 cm^{-1}. In the region of 1570-1437 cm^{-1}, the sharp and relatively strong peaks are attributed to the aromatic C-C of (pydc)$^{2-}$ ring that are also present in 1575-1458 cm^{-1} region of free pydcH$_2$.

The ^{1}H and ^{13}C NMR spectroscopy were applied as a tool for the structure determination of the proton transfer ion pair. In ^{1}H NMR spectrum, there are three clear characteristic sets of resonances at 8.11-8.407 ppm for hydrogens of (pydc)$^{2-}$ fragment. The other resonances, 7.27-6.91 ppm are attributed to the aromatic hydrogens of (phhyH)$^+$ and 4.67-3.69 ppm are related to the amine hydrogens of (phhyH)$^+$. The ^{13}C NMR spectrum shows seven resonances at 115.48, 123.78, 127.71, 129.68, 145.36, 145.97 and 164.90 ppm. According to peak

921

assignments reported for (pydc)$^{2-}$ [27], amongst the peaks mentioned above, the peaks at 115.48 ppm can be assigned to the carbon atom bound to NH group and 123.78, 129.68 and 145.97 ppm to other carbon atoms of (phhyH)$^{+}$. The other resonances, *i.e.* 127.71 and 145.36 ppm are related to the aromatic carbon atoms and 164.90 ppm to COO^{-} carbon atom of (pydc)$^{2-}$.

Characterization of (phhyH)[Ni(pydc)(pydcH)]· 3H$_2$O, 2

In IR spectroscopy of the dark green crystalline compound, a broad and strong bond in 3070-2831 cm^{-1} region and strong peaks in 1539 and 1624 cm^{-1} are attributed to stretching and bending vibrations of NH$_3^+$ group, respectively. The bands in 2470-3310 cm^{-1} region can be attributed to aromatic N-H stretching vibration. Also, some strong peaks in 1590 cm^{-1}, together with a strong peak in 1394 cm^{-1}, are due to the asymmetric and symmetric stretching vibrations of COO^{-} group, respectively.

One of the features of IR data of the nickel(II) compound is the separation between v_{as}(COO^{-}) and v_s(COO^{-}) that has been often used to diagnose the coordination modes in the carboxylate ligands [28]. The separation for unidentate carboxylato groups is >200 cm^{-1}, whereas it is <200 cm^{-1} in the bidentate ones [28,29]. Thus, the separation of 257 cm^{-1} in the present nickel(II) compound indicated a unidentate coordination mode for the coordinated carboxylate groups.

In ^{1}H NMR, compared with the spectrum of the proton transfer ion pair given in 3.1, the proton resonances appeared at 8.20 ppm for (pydc)$^{2-}$ and at 7.35-7.16, 6.87, 6.40 and 3.74 ppm for (phhyH)$^{+}$. In ^{13}C NMR spectrum, compared with the spectrum of the ion pair given in 3.1, the resonances at 114.39, 121.19, 129.38 and 148.57 ppm are assigned to (phhyH)$^{+}$. The remaining ^{13}C NMR resonances (128.00, 145.49 and 165.94 ppm) clearly indicate the presence of (pydc)$^{2-}$.

The UV spectrum of aqueous solution of (phhyH)$_2$(pydc) shows only one band, illustrated in Fig. 1. The absorption with a maximum at 275 nm can be assigned to n→π* transition of carboxyl C=O of (pydc)$^{2-}$ group. In the spectrum of (phhyH)[Ni(pydc)(pydcH)].3H$_2$O, the same absorption, centered at 280 nm, denotes the presence of the same group with some differences (Fig. 1). It can be interpreted as the negative charge focused on carboxyl oxygen atom of (pydc)$^{2-}$
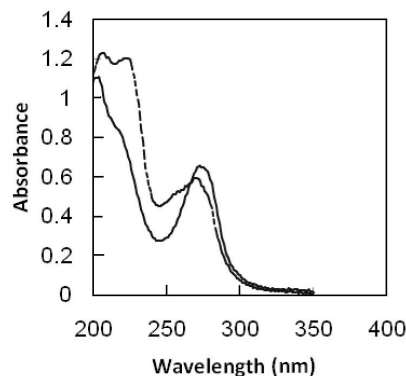
Fig. 1. The UV spectra of (phhyH)$_2$(pydc), **1** and (phhyH)[Ni(pydc)(pydcH)]·3H$_2$O, **2**: (----) (phhy)[Ni (pydc)(pydcH)], (——) phhy-pydc.

fragment of (phhyH)$_2$(pydc). However, in (phhyH)[Ni(pydc) (pydcH)].3H$_2$O, where (pydc)$^{2-}$ is coordinated to nickel(II) ion, the n→π* transitions of carboxyl O atoms are involved in coordination and the band is shifted to lower wavelengths (270 nm).

X-Ray Crystallographic Structure of (phhyH) [Ni(pydc)(pydcH)]·3H$_2$O, 2

The crystallographic data, selected bond lengths, bond angles, torsion angles and intermolecular hydrogen bond distances of the nickel(II) compound are presented in Tables 1, 2 and 3, respectively. The molecular structure diagram with hydrogen bonds, water clusters, the shortest distance between the closest parallel π-rings and the packing diagram of the structure are shown in Figs. 2, 3, 4 and 5, respectively.

All the above data reveal that nickel(II) atom is six coordinated by two tridentate (pydc)$^{2-}$ and (pydcH$^-$ groups and each [Ni(pydc)(pydcH)]$^-$ unit is accompanied by one (phhyH)$^{+}$ as counter ion and four water molecules (see Fig. 2).

The metal center is surrounded by four oxygen atoms O1, O3, O5 and O7 in equatorial and two pyridine nitrogen atoms N1 and N2 in axial positions. An examination of the angles O1-Ni1-O3 and O5-Ni1-O7 which equal to 156.00(8)° and 155.08(8)°, respectively (Table 2), reveals that the oxygen atoms form a flattened tetrahedral around the central atom. The values of O5-Ni1-O1-C6 and O1-Ni1-O7-C14 torsion angles 93.88(19)° and -103.71(19)°, respectively, and O1-Ni1-O7 and O3-Ni1-O5 bond angles 94.32(8)° and 91.29(8)°,

Table 1. Crystal Data and Structure Refinement for Compound 2

Compound	(phhyH)[Ni(pydc)(pydcH)]·3H$_2$O
Empirical formula	C$_{20}$H$_{22}$N$_4$NiO$_{11}$
Formula weight	553.12
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
Unit cell dimensions	*a* = 15.094(2) Å *β* = 103.948(3)°
	b = 19.992(3) Å
	c = 7.5942(10) Å
Volume	2224.0(5) Å^3
Z	4
Density (calculated)	1.649 mg m^{-3}
Absorption coefficient	0.944 mm^{-1}
F(000)	1144
Crystal size	0.34 × 0.18 × 0.17 mm^3
Theta range for data collection	1.72 to 26.00°
Index ranges	-18 <= h <= 18, -24 <= k <= 24, -9 <= l <= 9
Reflections collected	19593
Independent reflections	4379 [*R*(int) = 0.0480]
Observed reflections [I > 2sigma(I)]	3265
Completeness to theta = 26.00°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.856 and 0.823
Refinement method	Full-matrix least-squares on *F*2
Data/restraints/parameters	4379/0/325
Goodness-of-fit on F2	1.015
Final *R* indices [I > 2sigma(I)]	*R*1 = 0.0412, w*R*2 = 0.0843
R indices (all data)	*R*1 = 0.0591, w*R*2 = 0.0911
Largest diff. peak and hole	0.908 and -0.352 e.Å^{-3}

respectively (see Table 2), show that (pydc)$^{2-}$ and (pydcH)$^-$ units are almost perpendicular to each other. Therefore, the coordination sphere around nickel(II) is a distorted octahedral with N$_1$-Ni$_1$-N$_2$ angle equal to 171.35(9)° (see Table 2).

There are four carboxylate groups around the metal center. Obviously, among C-O bonds of each carboxylate group, the bond containing coordinated oxygen atom is longer than the other. For instance, as shown in Table 2, comparing C6-O1 with C6-O2, C7-O3 with C7-O4, C14-O7 and C14-O8 bonds shows that in each pair, the former which contains the

coordinated oxygen atom is longer. On the contrary, between C13-O5 and C13-O6, the bond containing the coordinated oxygen atom is shorter. This is due to the presence of acidic hydrogen atom on O6 and lack of double CO bond. The torsion angles given in Table 2, demonstrate that the (COO)$^-$ and COOH groups are almost coplanar with the corresponding pyridine rings.

There are varieties of O-H⋯O and N-H⋯O hydrogen bonds between H$_2$O molecules, cationic and anionic moieties in the compound which are classified as strong hydrogen

923

**Table 2.** Selected Bond Lengths, Bond Angles, Torsion Angles (Å, °)

|			
Ni1-N2	1.969 (2)	Ni1-O1	2.114 (2)
Ni1-N1	1.970 (2)	Ni1-O7	2.121 (2)
Ni1-O3	2.111 (2)	Ni1-O5	2.192 (2)
O1-C6	1.280 (3)	O2-C6	1.237 (3)
O3-C7	1.278 (3)	O4-C7	1.238 (3)
O5-C13	1.227 (3)	O6-C13	1.298 (3)
O7-C14	1.265 (3)	O8-C14	1.251 (3)
N2-Ni1-N1	171.35 (9)	O3-Ni1-O7	94.21 (8)
N2-Ni1-O3	100.05 (8)	O1-Ni1-O7	94.32 (8)
N1-Ni1-O3	77.76 (8)	N2-Ni1-O5	76.88 (8)
N2-Ni1-O1	103.64 (9)	N1-Ni1-O5	94.74 (8)
N1-Ni1-O1	78.25 (8)	O3-Ni1-O5	91.29 (8)
O3-Ni1-O1	156.00 (8)	O1-Ni1-O5	90.35 (8)
N2-Ni1-O7	78.23 (9)	O7-Ni1-O5	155.08 (8)
Ni1-O1-C6-O2	-178.0 (2)	Ni1-O5-C13-O6	175.5 (2)
Ni1-O3-C7-O4	172.2 (2)	Ni1-O7-C14-O8	177.3 (2)

Table 3. Hydrogen Bonds Geometry (Å, °)

D-H⋯A	D-H	H⋯A	D⋯A	<D-H⋯A
N3-H1⋯O3W[i]	0.98	2.05	2.961 (3)	154
N4-H2⋯O8[ii]	0.96	1.77	2.688 (3)	160
N4-H3⋯O1	0.92	1.83	2.733 (3)	168
N4-H4⋯O2[iii]	0.99	1.78	2.743 (3)	164
O1W-H5⋯O3W[iv]	0.91	1.97	2.818 (3)	156
O1W-H6⋯O4	0.92	1.99	2.872 (3)	162
O2W-H7⋯O4[v]	0.92	1.83	2.742 (3)	169
O2W-H8⋯O3	0.88	1.84	2.714 (3)	177
O3W-H9⋯O1W[vi]	0.82	1.98	2.787 (3)	169
O3W-H10⋯O8[vii]	0.99	1.92	2.871 (3)	159
O6-H11⋯O2W[ii]	0.77	1.73	2.506 (3)	175
C4-H4A⋯O5[v]	0.95	2.49	3.327 (4)	147
C9-H9A⋯O2W[viii]	0.95	2.58	3.529 (4)	174
C18-H18A⋯O2[ix]	0.95	2.57	3.308 (4)	134

Symmetry codes: (i) -x+1, y-1/2, -z+3/2; (ii) x, y, z+1; (iii) -x, -y+1, -z+2; (iv) x, -y+3/2, z+1/2; (v) x, -y+3/2, z-1/2; (vi) x, y, z-1; (vii) -x+1, y+1/2, -z+1/2; (viii) -x+1, -y+1, -z+2; (ix) -x, -y+1, -z+1.
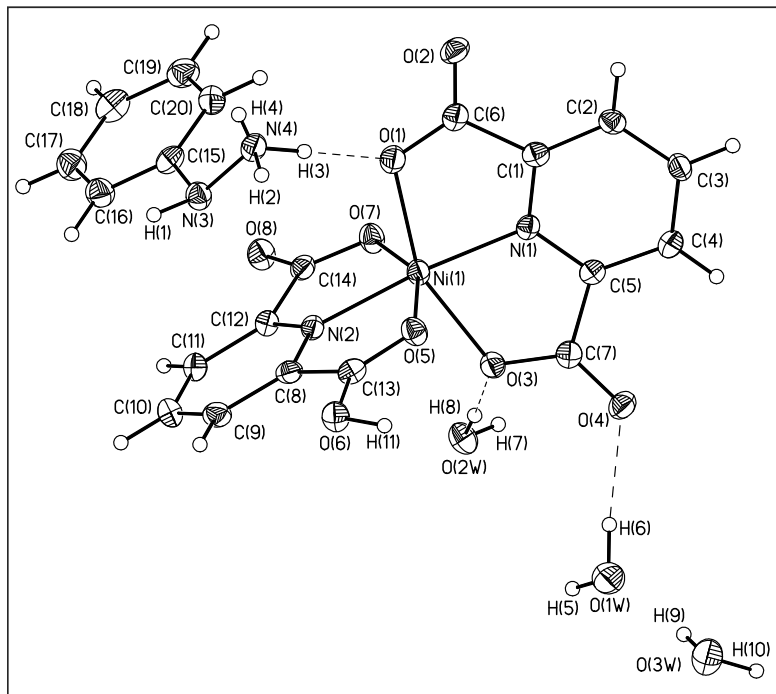
Fig. 2. Molecular structure of (phhyH)[Ni(pydc)(pydcH)]·3H$_2$O, **2**.
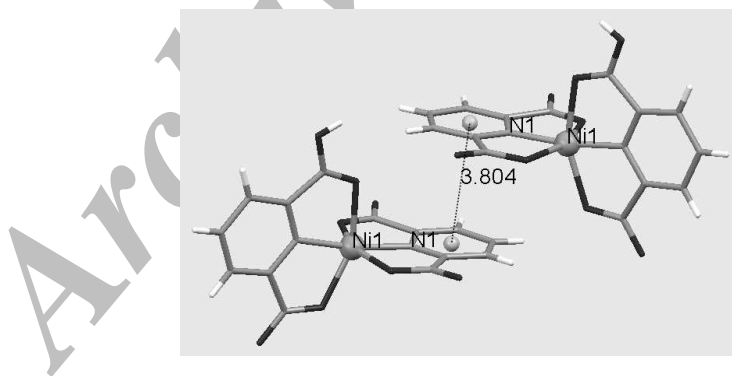
Fig. 3. Representation of π-π stacking in (phhyH)[Ni(pydc)(pydcH)]·3H$_2$O, **2**.

bonds [35] (Table 3). The hydrogen bond between H$_2$O molecules leads to a chain water cluster illustrated in Fig. 3. Moreover, C-H···O hydrogen bonds, that are classified as weak hydrogen bonds, are observed in the structure [30]. As displayed in Table 3, the strongest C-H···O hydrogen bond is C18-H18A···O2. The distances between (pydc)$^{2-}$ rings in the neighboring molecules are measured as 3.804 Å (the last is shown in Fig. 4). These distances categorized as π-π stacking, in addition to C-O···π, van der Waals and dipole-dipole interactions, seem to be effective in stabilizing the crystal structure and crystal packing shown in Fig. 5. All the above interactions take part in the formation of a supramolecular
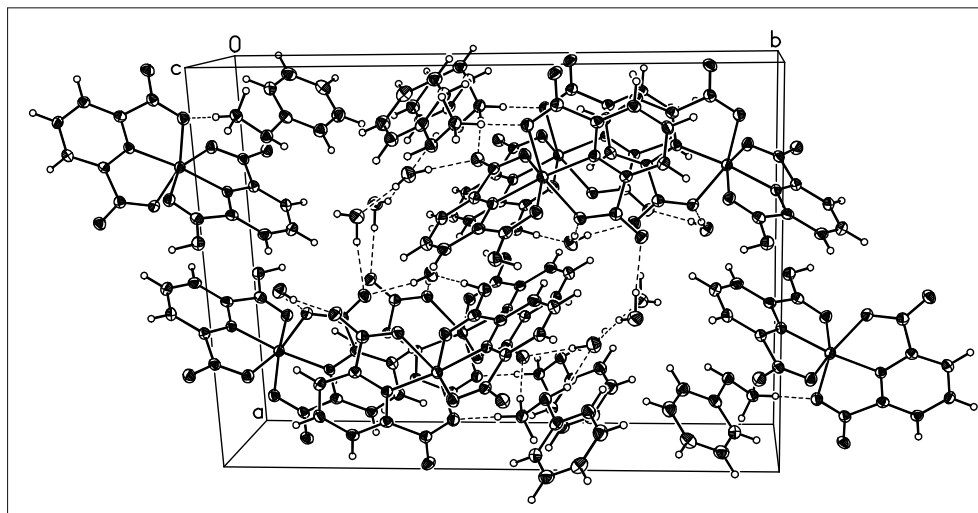
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Fig. 4. The crystal packing of **2** showing hydrogen bonds as dashes.

Table 4. Overall Stability and Stepwise Protonation Coststants of pydc and phhy and Recognition Constants for Interaction Between them in Aqueous Solution at 25 °C and $\mu = 0.1$ M NaNO$_3$

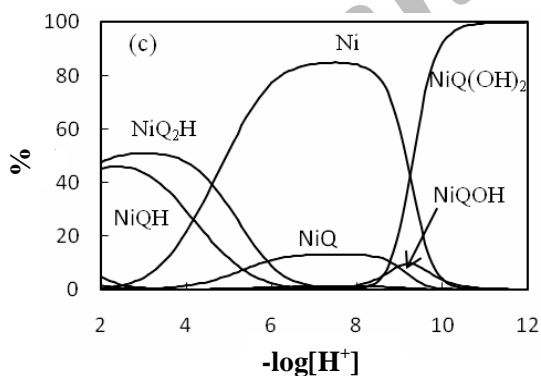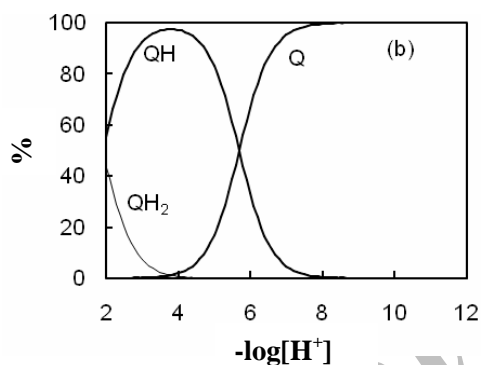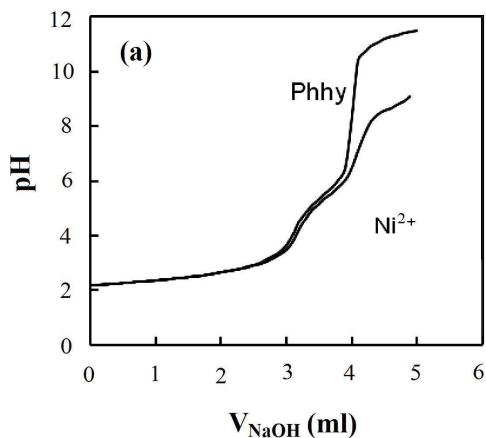| Stoichiometry			logβ	Equilibrium quotient K	logK	Max (%)	at pH
phhy	pydc	h					
0	1	1	4.81	-	4.81	89	3.6
0	1	2	7.19	-	2.38	55.8	2
0	1	3	8.76	-	1.57	20.9	2
1	0	1	5.70	-	5.70	97.5	3.8
1	0	2	7.60	-	1.9	44.6	2
1	1	1	9.58	[phhypydcH]/[phhyH][pydc]	3.88	64.7	5.7
				[phhypydcH]/[phhy][pydcH]	4.77		
1	1	2	14.26	[phhypydcH$_2$]/[phhyH][pydcH]	3.75	63.2	3.7-3.8
1	1	3	16.86	[phhypydcH$_3$]/[phhyH$_2$][pydcH]	4.45	58.9	2
				[phhypydcH$_3$]/[phhyH][pydcH$_2$]	3.97		

structure.

Solution Study of (phhyH)$_2$(pydc), 1 and (phhyH)[Ni(pydc)(pydcH)]·3H$_2$O, 2

In this section, primarily the fully protonated forms of pydc (L) and phhy (Q) were titrated with a standard NaOH solution in order to obtain some information about their protonation constants as the building blocks of the pydc-phhy proton transfer system. The protonation constants of pydc [31,32] and phhy were calculated by fitting the volume-pH
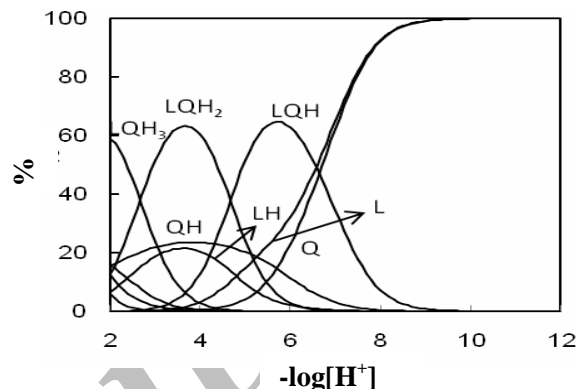
data (Fig. 5a) to the BEST program. It is noteworthy that the resulting protonation constant values were in satisfactory agreement with those reported for phhy [37] in the literature; the observed difference being caused by different conditions.

The evaluation of the equilibrium constants for the interaction between pydc and phhy in different protonation forms was carried out through compariing the calculated and experimental pH profiles, obtained with both pydc and phhy present [38,39,40]. The distribution diagrams for phhy are shown in Fig. 5b. The results are shown in Table 4. The
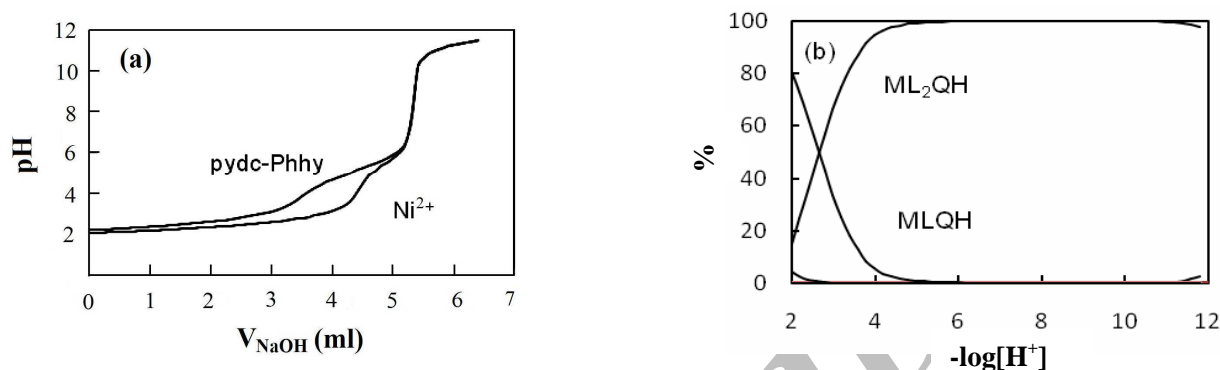
926

Fig. 6. Distribution diagram of proton transfer interaction between phhy (Q) and pydc (L).

corresponding species distribution diagram for pydc-phhy is shown in Fig. 7. The two binding constants for the binary species formed from the pydc and phhy are listed in Table 4. As it is obvious, the most abundant proton-transfer species present at pH 5.7 (64.7%), at pH 3.7-3.8 (63.2%) and 2.0 (58.9%) are pydc-phhyH (logK = 3.88), pydcH-phhy (logK = 4.77), pydcH-phhyH (logK= 3.75), pydcH-phhyH$_2$ (logK = 4.45) and pydcH$_2$-phhyH (logK = 3.97).

In order to evaluate the stoichiometry and stability of Ni^{2+} complex with pydc-phhy proton transfer system in aqueous solution, the equilibrium potentiometric pH titration profiles of pydc [32], phhy and their 1:1 mixture were obtained in the absence and presence of the Ni^{2+} ion. The resulting pH profiles are shown in Figs. 5a and 7a. It can be seen that the titration of ligand in the presence of Ni^{2+} ion stopped when the precipitate was observed. It was found that, there was a weak interaction between phhy and Ni^{2+} ion, but the titration curves of pydc and pydc-phhy in the presence of the cited metal ion were depressed considerably. The cumulative stability constants of M$_m$L$_l$Q$_q$H$_h$, β_{mlqh}, are defined in our previous publications [31,32]. M, L, Q and H are metal ion, pydc, phhy and proton, respectively, and m, l, q, and h are the respective stoichiometric coefficients.

The cumulative stability constants were evaluated by fitting the corresponding pH titration curves into the BEST program. The resulting values for the most likely complexed species in aqueous solutions are included in Table 5, and the corresponding distribution diagrams are shown in Figs. 5c and

Fig. 5. Potentiometric titration curves of phhy (a) in the absence and presence of Ni^{2+} ions with NaOH 0.09623 M in aqueous solution at 25 °C and μ = 0.1 M NaNO$_3$ and distribution diagrams of phhy(Q) (b) and Distribution diagrams of phhy(Q)/Ni^{2+} binary systems (c).

927

Fig. 7. Potentiometric titration curves of pydc+phhy in the absence and presence of Ni^{2+} ions with NaOH 0.09623 M in aqueos solution at 25 °C and μ = 0.1 M NaNO$_3$, (a) and distribution diagrams of pydc(L)/phhy(Q)/Ni^{2+} ternary system.

Table 5. Overall Stability Constants of PhHy/pydc/Ni^{2+} (q/l/m) Binary and Ternary Systems in Aqueous Solution at 25 °C and μ = 0.1M NaNO$_3$

System	m	l	q	h	logβ	Max%	at pH
Ni-PhHy	1	0	1	0	1.83	13.15	7.5
	1	0	1	1	7.11	45.89	2.2
	1	0	1	2	8.11	1.58	2.0
	1	0	2	0	3.38	1.06	3.0-3.1
	1	0	2	1	10.54	50.92	7.6-7.8
	1	0	2	2	11.54	4.97	2.0
	1	0	1	-1	-7.38	9.67	9.0
	1	0	1	-2	-15.75	100.00	12.0
Ni-pydc-PhHy	1	1	1	0	8.65	Negligible	-
	1	1	1	1	23.56	80.48	2
	1	1	1	2	24.31	4.48	2
	1	2	1	0	13.24	Negligible	-
	1	2	1	1	29.72	99.95	>8.2

7b. Our group has reported the complexation of Ni^{2+} with pydc elsewhere [41]. These results reveal that, Ni^{2+} ion forms relatively stable complexes with pydc and pydc-phhy systems and less stable ones with phhy.

As observed in Fig. 5c and Table 5 concerning the results of phhy-Ni^{2+} ion system, the most likely species for this system are: NiQ, NiQ$_2$, NiQOH, NiQH, NiQH$_2$, NiQ$_2$H, NiQ$_2$H$_2$, NiQOH and NiQ(OH)$_2$. Furthermore, Fig. 7b and

Table 5 reveal the formation of a variety of ternary complexes between Ni^{2+} and the proton-transfer system at different ranges of pH. The predominant species are: NiLQH (at pH 2.0) for NiLQH$_2$ (at pH 2.0), and for NiL$_2$QH (at pH > 8.2). It is interesting to note that the stoichiometries of NiL$_2$QH with the most abundant solution are very similar to that reported for the corresponding isolated complex in the solid state.

928

SUPPLEMENTARY MATERIAL

Crystallographic data for the title structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC 757935 for $C_{20}H_{22}N_4NiO_{11}$. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code+ (1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

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929

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930