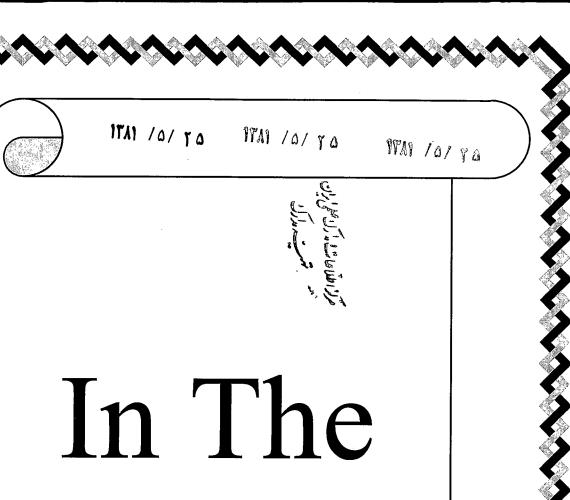
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PREPARATION AND CHARACTERIZATION OF A NOVEL SELF-ASSEMBLING SYSTEM CONTAINING PYRIDINE RING AND ITS COMPLEXES WITH METAL IONS, AND SYNTHESIS OF TWO MACROCYCLIC LIGANDS DERIVED FROM PYRIDINE

Under Supervision of:

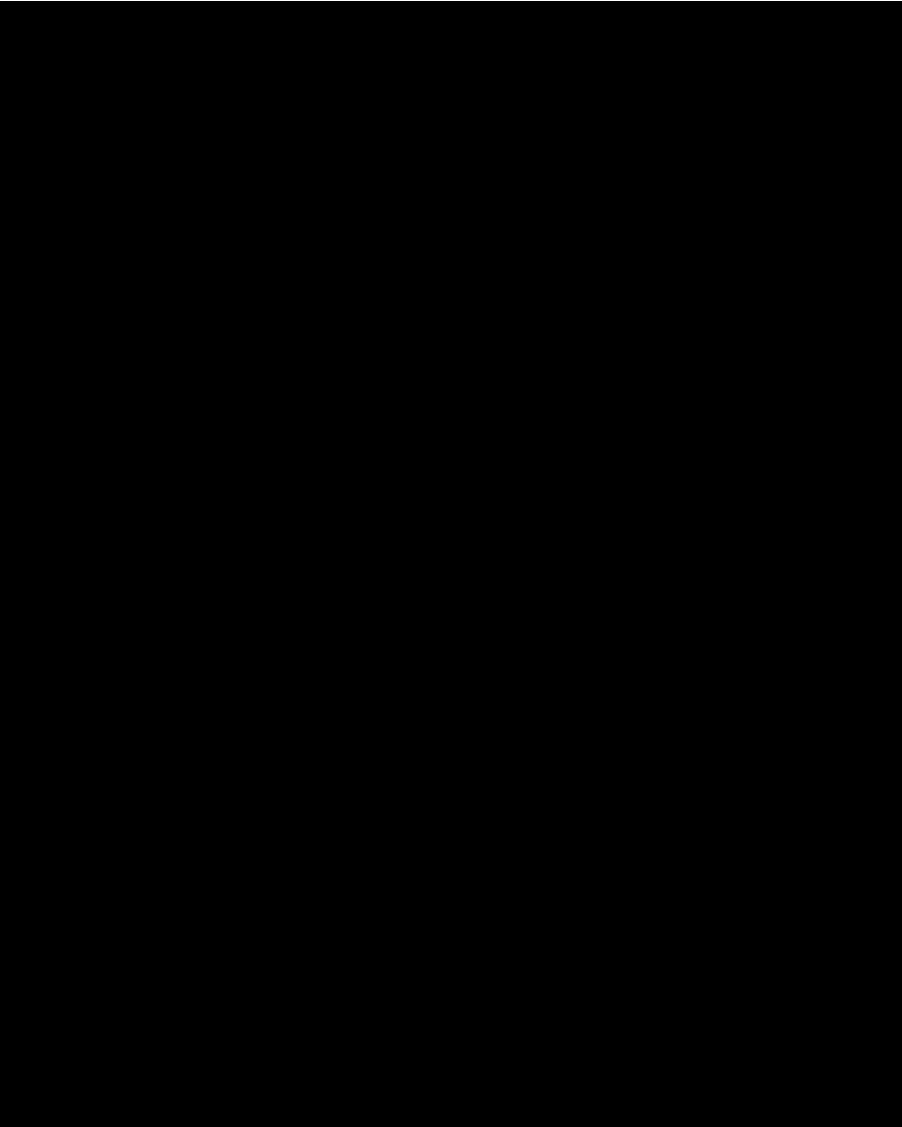
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PREPARATION AND CHARACTERIZATION OF A NOVEL SELF-ASSEMBLING SYSTEM CONTAINING PYRIDINE RING AND ITS COMPLEXES WITH METAL IONS, AND SYNTHESIS OF TWO MACROCYCLIC LIGANDS DERIVED FROM PYRIDINE

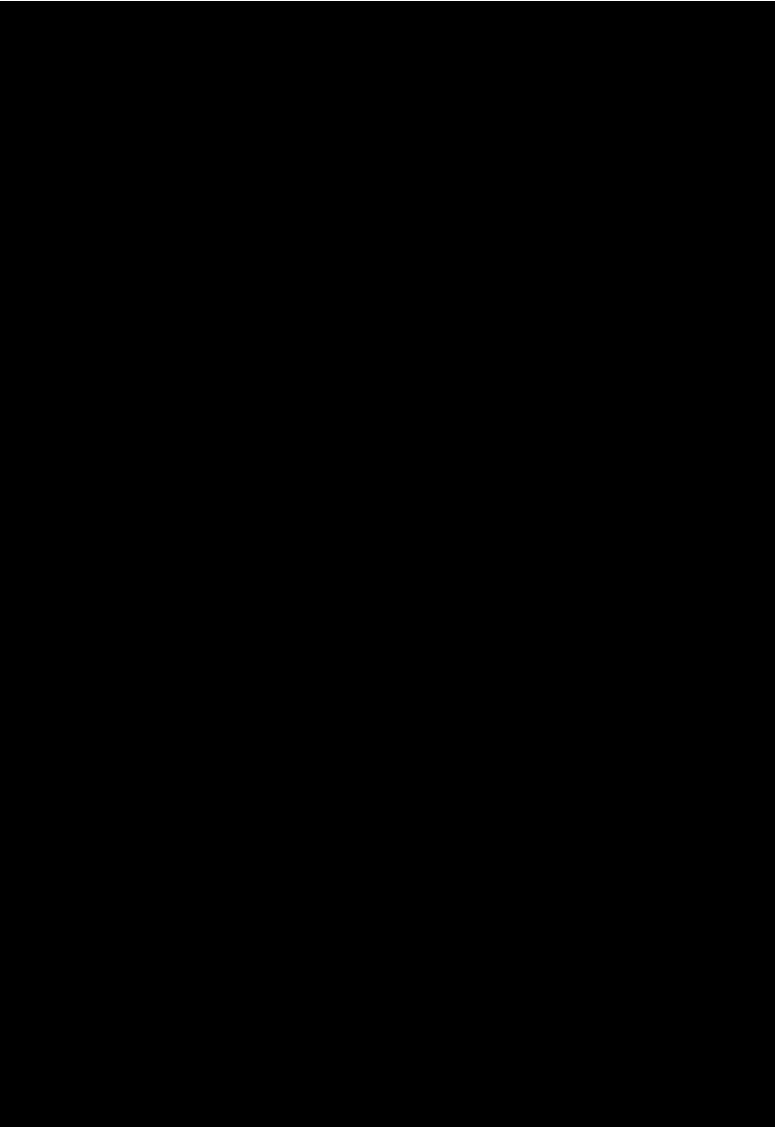
ABSTRACT

The reaction of 2,6-pyridinedicarboxylic acid, [pydc.H₂] with 2,6-pyridinediamine, [pyda], in THF in the presence of Et₃N leads to the formation of a novel self-assembling system LH₂, [pyda.H₂]²⁺[pydc]²⁻. The characterization was performed using EI, CI, ES mass spectroscopy as well as 1 H and 13 C solution NMR and X-ray crystallography. The intermolecular forces in this novel system consists of H-bonding and ion-pairing simultaneously. The 13 C solid phase NMR data is in agreement with X-ray crystal structure. As expected, the [pydc]²⁻ unit in the solid phase 13 C NMR shows twice peaks as in solution. Spectrophotometric studies in aqueous solutions supported the formation of 1:1 adduct L with a formation constant of logK_f = 5.65 ± 0.13.

One equivalent of metal ions such as Cr(III), Co(II), Ni(II), Cu(II), Zn(II), with two equivalent of LH₂, results in the formation of [pyda.H][Cr(pydc)₂].pydc.H₂, H₂O (space group: $P2_1/c$; Z=8; $R_1=0.0574$; $wR_2=0.1310$; C.N. = 6; distorted O_h; mononuclear), [pyda.H]₂[M(pydc)₂].H₂O, {M = Co(II), Ni(II), Cu(II)} (space group: $P2_1/n$; Z=4; $R_1=0.0482$, 0.0444, 0.0476 respectively; $wR_2=0.1230$, 0.12290.0957 respectively; C.N. = 6; distorted O_h; mononuclear) and [pyda.H][Zn(pydc)(pydc.H)].3H₂O (space group: $P\overline{1}$; Z=2; $R_1=0.0401$; $wR_2=0.0857$; C.N. = 6; distorted O_h; mononuclear). The characterization was performed using elemental analysis, IR, ¹H and ¹³C solution NMR spectroscopy as well as X-ray crystallography. The ESI/MS data was also applied for Co(II) and Ni(II) complexes.

The complexation reaction between LH₂ and Cd(II) and Hg(II) salts results in the formation of [Cd(pydc)(H₂O)₃]₂.2[pydc.H₂] (space group: $P2_1/c$; Z = 2; $R_1 = 0.0382$; $wR_2 = 0.0860$; C.N. = 7; distorted pentagonal bipyramidal; binuclear) and {[pyda.H]₂[HgCl₂ (pydc)₂]}_n (space group: $P\overline{1}$; Z = 1; $R_1 = 0.0639$; $wR_2 = 0.1382$; C.N. = 6; distorted O_h; polymer).

The reaction between Zr(IV) salt and LH₂ results in the formation of crystalline product. It is a novel self-assembling system [pyda.H] NO₃ free from zirconium



(space group: $P2_1$; Z = 2; $R_1 = 0.0477$; $wR_2 = 0.1176$; $\pi - \pi$ stacking between pyridines rings).

The reaction between PdCl₂ and LH₂ in CH₃CN results in the formation of [pyda.H]₂[PdCl₄] (space group: PT; Z = 1; $R_1 = 0.0602$; $wR_2 = 0.1465$; C.N. = 4; square planer), and presumably [Pd(pydc.H)₂].xH₂O and [pyda.H][Pd(pydc)(pydc.H)].H₂O complexes. The ¹H, ¹³C NMR, IR and ESI/MS spectra and confirmed the formation of these complexes.

The reaction of LH₂ with La(NO₃).6H₂O affords to the formation of an anionic La(III) complex, [pyda.H]₂[La(H₂O)₂(pydc)₂]₂ (space group: P_{1} ; Z = 1; $R_{1} = 0.0442$, $wR_{2} = 0.0992$; C.N. = 9; highly distorted tricapped trigonal prism; binuclear).

The complexation reaction between LH_2 and Pb(II) ion, leads to the formation of $\{[Pb(pydc)(pydc.H_2)(H_2O)_2]_2\}_n$ (space group: $P_{\overline{1}}$; Z=2; $R_1=0.0373$; $wR_2=0.0914$; C.N. = 6; distorted O_h ; polymer; π - π stacking between pyridines rings; the lone pair of electrons on Pb(II) is presumably stereochemically active and the structure is hemidirected)

The reaction of LH₂ with bismuthsubnitrate results in the formation of $\{[BiCl(H_2O)(pydc)]_2\}_n$ (space group: $P2_1/c$; Z=2; $R_1=0.0314$; $wR_2=0.0809$; C.N. = 7; distorted pentagonal bipyramidal; polymer).

Among the characterization methods applied to the synthesis of complexes, solution NMR and MS were found to be suitable techniques in order to check the existence of the cationic $[pyda.H_2]^+$ unit in the complexes.

2,10,16,24-tetraoxo-3,6,9,17,20,23-hexaoxa-29, 30-diaza-tricyclo [23.3.1.1^{11,15}] triacontane- 11,13,25,27,29,30-hexaene, **I**, was synthesized through the reaction between diethyleneglycol and 2,6-pyridinedicarbonyldichloride in the presence of Et₃N in benzene. The [2+2] polyether-tetraester macrocycle, **I**, was characterized by elemental analysis, IR, ¹H NMR, ¹³C NMR, EI/MS, and ESI/MS spectroscopy. The M+1 peak in ESI/MS spectrum at m/z 475.1 was strongly in support of the formation of [2+2] macroheterocycle.

1,10,17,26-tetraoxo-2,9,18,25-tetraoxa[2.2.2.2](2,6)pyridineophen, II, was synthesized by the similar reaction between 2,6-pyridinedicarbonyldichloride and 2,6-pyridinediamine in benzene. The [2+2] tetraomide macrocycle II, was characterized by elemental analysis and IR spectroscopy. The solid compound, II, is insoluble in most of the common solvents.

Section 1

2,6—Pyridinedicarboxylic acid and 2,6—pyridinediamine complexes

The complexation of metal ions by 2,6-pyridinedicarboxylic acid [pydc.H₂] has been extensively studied. This terms mainly from its ability to form stable chelates [1], with various coordination modes such as bidentate [2] meridian [3], or bridging [4]. Other interesting properties are its biological activity [5], its ability to stabilize unusual oxidation states [6] and its usefulness in analytical chemistry [7] such as chemical analysis of iron at low concentration (down to 4 ppm) [7a], in corrosion inhibition [8] and in decontamination of nuclear reactors [9].

The structural characterization of the 1:2 divalent metal complexes of 2,6-pyridinedicarboxylic acid [pydc.H₂] have shown that they formed neutral, monoanionic [pydc.H]⁻, and dianionic [pydc]²⁻ ligand molecules and could accordingly be formulated as [M(pydc)(pydc.H₂)].xH₂O or [M(pydc.H)₂].xH₂O. The reaction of Co(II), Ni(II) carbonates or hydroxides with aqueous solution of [pydc.H₂] affords the complexes [M(pydc.H)₂].3H₂O, M = Ni(II), Co(II), Cu(II) and Zn(II). A single crystal X-ray analysis on [Ni(pydc.H)₂].3H₂O, provided unambiguous evidence for the formulation of the Ni(II) complex, involving two equivalent tridentate monoanionic [pydc.H]⁻ ligand molecules, rather than the alternative of