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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 :

Prof. Hossein Aghabozorg
Prof. Abolghasem Moghimi

By:

Maryam Ranjbar

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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.H_2] with 2,6–pyridinediamine, [pyda], in THF in the presence of Et_3N leads to the formation of a novel self–assembling system $\mathbf{LH_2}$, $[pyda.H_2]^{2+}[pydc]^{2-}$. The characterization was performed using EI, CI, ES mass spectroscopy as well as ^1H 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 $\log K_f = 5.65 \pm 0.13$.

One equivalent of metal ions such as Cr(III), Co(II), Ni(II), Cu(II), Zn(II), with two equivalent of $\mathbf{LH_2}$, results in the formation of [pyda.H][Cr(pydc)$_2$].pydc.H_2, H_2O (space group: $P2_1/c$; Z = 8; R_1 = 0.0574; wR_2 = 0.1310; C.N. = 6; distorted O_h; mononuclear), $[pyda.H]_2[M(pydc)_2].H_2O$, {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)].$3H_2O$ (space group: $P\bar{1}$; 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 ^{13}C 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 $\mathbf{LH_2}$ and Cd(II) and Hg(II) salts results in the formation of $[Cd(pydc)(H_2O)_3]_2.2[pydc.H_2]$ (space group: $P2_1/c$; Z = 2; R_1 =0.0382; wR_2 = 0.0860; C.N. = 7; distorted pentagonal bipyramidal; binuclear) and $\{[pyda.H]_2[HgCl_2\ (pydc)_2]\}_n$ (space group: $P\bar{1}$; Z = 1; R_1 = 0.0639; wR_2 = 0.1382; C.N. = 6; distorted O_h; polymer).

The reaction between Zr(IV) salt and $\mathbf{LH_2}$ results in the formation of crystalline product. It is a novel self–assembling system [pyda.H] NO_3 free from zirconium

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

The reaction between $PdCl_2$ and **LH_2** in CH_3CN results in the formation of $[pyda.H]_2[PdCl_4]$ (space group: $P\bar{1}$; Z = 1; R_1=0.0602; wR_2=0.1465; C.N. = 4; square planer), and presumably $[Pd(pydc.H)_2].xH_2O$ and $[pyda.H][Pd(pydc)(pydc.H)].H_2O$ complexes. The ^1H, ^{13}C NMR, IR and ESI/MS spectra and confirmed the formation of these complexes.

The reaction of **LH_2** with $La(NO_3).6H_2O$ affords to the formation of an anionic La(III) complex, $[pyda.H]_2[La(H_2O)_2(pydc)_2]_2$ (space group: $P\bar{1}$; 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: $P\bar{1}$; 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 **LH_2** 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 Et_3N in benzene. The [2+2] polyether-tetraester macrocycle, **I**, was characterized by elemental analysis, IR, ^1H NMR, ^{13}C 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-tetraaza[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] tetraamide macrocycle **II**, was characterized by elemental analysis and IR spectroscopy. The solid compound, **II**, is insoluble in most of the common solvents.

CHAPTER 1

Section 1

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

The complexation of metal ions by 2,6–pyridinedicarboxylic acid [pydc.H_2] 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.H_2] have shown that they formed neutral, monoanionic $[pydc.H]^-$, and dianionic $[pydc]^{2-}$ ligand molecules and could accordingly be formulated as $[M(pydc)(pydc.H_2)].xH_2O$ or $[M(pydc.H)_2].xH_2O$. The reaction of Co(II), Ni(II) carbonates or hydroxides with aqueous solution of [pydc.H_2] affords the complexes $[M(pydc.H)_2].3H_2O$, M = Ni(II), Co(II), Cu(II) and Zn(II). A single crystal X–ray analysis on $[Ni(pydc.H)_2].3H_2O$, 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