

## Two Novel Metal Organic Frameworks of Sn(II) and Pb(II) with Pyridine-2,6-dicarboxylic Acid and 4,4'-Bipyridine: Syntheses, Crystal Structures and Solution Studies

J. Soleimannejad<sup>a</sup>, H. Aghabozorg<sup>b,\*</sup>, S. Hooshmand<sup>a</sup>, M. Ghanbari<sup>c</sup>, F. Manteghi<sup>d</sup> and M. Shamsipur<sup>c</sup>

<sup>a</sup>Department of Chemistry, Ilam University, Ilam, Iran

<sup>b</sup>Faculty of Chemistry, Tarbiat Moallem University, Tehran, Iran

<sup>c</sup>Department of Chemistry, Razi University, Kermanshah, Iran

<sup>d</sup>Department of Chemistry, Iran University of Science and Technology, Tehran, Iran

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Two novel compounds with formulae  $[\text{Sn}_2(\text{pydcH})_2(\text{H}_2\text{O})_2\text{O}]_n$ , **1**, and  $(4,4'\text{-bpyH}_2)_{0.5}[\text{Pb}(\text{pydc})_2(4,4'\text{-bpyH})] \cdot 4,4'\text{-bpy} \cdot 4\text{H}_2\text{O}$ , **2**, were obtained from a one-pot reaction between pyridine-2,6-dicarboxylic acid ( $\text{pydcH}_2$ ) and 4,4'-bipyridine (4,4'-bpy) with corresponding Sn(II) and Pb(II) salts. In compound **1** with a polymeric structure, each Sn(II) atom is six-coordinated by one water molecule, two  $(\text{pydcH})^-$  groups and one oxide group resulted in a coordination polymer. Compound **2** has a seven-coordinated environment around Pb(II) atom by two  $(\text{pydc})^{2-}$  groups and one (4,4'-bpyH). The anionic complex is balanced by half a  $(4,4'\text{-bpyH}_2)^{2+}$  as counter ion. There are four uncoordinated water molecules and one 4,4'-bpy in the crystal lattice. Therefore, in compound **2**, we have neutral, mono- and biprotonated forms of 4,4'-bipyridine, simultaneously. Several interactions including O-H $\cdots$ O, O-H $\cdots$ N and C-H $\cdots$ O hydrogen bonds, ion pairing, C-O $\cdots$  $\pi$  (O $\cdots$ Cg 3.324(3) Å and 3.381(3) Å in **1** and O $\cdots$ Cg 3.346(4) Å in **2**), C-H $\cdots$  $\pi$  (C $\cdots$ Cg 3.618(4) Å in **2**), and  $\pi\cdots\pi$  stackings (with Cg $\cdots$ Cg distances of 3.613(2) and 3.641 (2) Å in **2**) are present to expand and stabilize the structure. The complexation reactions of bpy and pydc-bpy with  $\text{Sn}^{2+}$  and  $\text{Pb}^{2+}$  ions in aqueous solution were investigated by potentiometric pH titrations, and the resulting equilibrium constants and species distributions at various pHs for major formed complexes are described.

**Keywords:** Pyridine-2,6-dicarboxylic acid, 4,4'-Bipyridine, Sn(II) and Pb(II) complexes, Crystal structures, Solution studies

### INTRODUCTION

The rational design and synthesis of 3D architectures as well as molecular recognition are regarded as key aspects of modern coordination chemistry, not only because of their intriguing topologies but also because of their potential applications as functional materials [1]. Dicarboxylate ligands are widely used to assemble supramolecular network

organized by coordination bonds, hydrogen bonds and  $\pi$ - $\pi$  stacking interactions. On the other hand, the functional groups, flexibility, symmetry and configuration of the organic ligands also have significant effect on the structures of the complexes. Furthermore, the auxiliary ligands, such as 2,2'-bpy, 4,4'-bpy and phen (phenanthroline), have obviously great effect on the structures of complexes [2].

In continuation of our research on supramolecular systems, now we have found a certain route to combine a carboxylic acid with an amine to produce some almost water-soluble

\*Corresponding author. E-mail: aghabozorg@saba.tmu.ac.ir

self-associating ion pair systems, which react with metal ions and result in a wide variety of metal complexes [3].

Our main strategy in selecting the H-donor and H-acceptor building blocks was to choose: (i) those dicarboxylic acids that can function as multidentate ligands in metal complexation, (ii) donors and acceptors that are able to undergo intermolecular H-bonding and  $\pi$ - $\pi$  stacking and (iii) suitable donors and acceptors from the  $pK_a$  values to guarantee H-transfer [4]. Many systems applying different acids and amines such as (tataH<sub>2</sub>)(pydc), tata: 2,4,6-triamino-1,3,5-triazine (melamine) [5a], (tataH<sub>2</sub>)<sub>2</sub>(pydc) [5a], (creatH)(pydcH).H<sub>2</sub>O, creat: creatinine [5b], (pydaH)(pydcH), pyda: pyridine-2,6-diamine [5c], (NH<sub>4</sub>)(pydcH) [5d], (pnH<sub>2</sub>)(pydc).(pydcH<sub>2</sub>).2.5H<sub>2</sub>O, pn: propane-1,3-diamine [5e], (phenH)<sub>2</sub>(pydc), phen: 1,10-phenanthroline [5f], (pyrimH)[H(Hpydc)<sub>2</sub>], pyrim: *N,N'*-diethyl-2-amino-6-methyl-4-pyrimidinol [5g], and piperazine including (pipzH<sub>2</sub>)(py-2,5-dc).2H<sub>2</sub>O, py-2,5-dcH<sub>2</sub>: pyridine-2,5-dicarboxylic acid [6a], (pipzH<sub>2</sub>)(ox).H<sub>2</sub>O, oxH<sub>2</sub>: oxalic acid [6b], (pipzH<sub>2</sub>)(py-2,3-dcH)<sub>2</sub>, py-2,3-dcH<sub>2</sub>: pyridine-2,3-dicarboxylic acid [6c,d], (pipzH<sub>2</sub>)<sub>2</sub>(btc).6H<sub>2</sub>O, btcH<sub>4</sub>: benzene-1,2,4,5-tetracarboxylic acid [6e] were synthesized by our team. Although in all the cases mentioned above [5,6], the applied acids and amines were previously purchased, in the case of (pydaH<sub>2</sub>)(phencd), phencd = 1,10-phenanthroline-2,9-dicarboxylic acid, we used our own procedure to synthesize the acid [7]. Similar to the title compounds, other Sn(II) and Pb(II) compounds were synthesized and characterized as for [Sn(pydc)(OH)(H<sub>2</sub>O)( $\mu$ -OH)]<sub>2</sub>.4H<sub>2</sub>O [8], {[Pb(pydc)(pydcH<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>} [9].

## EXPERIMENTAL

### General Methods and Materials

Tin(II) chloride dihydrate (99%), lead(II) nitrate (99%), pyridine-2,6-dicarboxylic acid (97%) and 4,4'-bipyridine (99%) were all purchased from Merck. The X-ray data were obtained with a Bruker SMART Diffractometer. Single crystals of the compounds suitable for crystallography were selected. Unit cell determination and data about the compounds were collected on a Bruker SMART CCD area detector system [10] using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å).

The structures were solved and refined by full-matrix least-squares techniques on  $F^2$  using SHELX-97 (SHELXL

program package) [11,12]. The absorption corrections type was multi-scan. The hydrogen atoms of NH<sub>2</sub> groups and water molecules were found in different Fourier syntheses. The H(C) atom positions were calculated. 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 corresponding H atoms are bonded. Refinement of  $F^2$  was against all reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  were based on  $F^2$ , conventional  $R$ -factors were based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  was used only for calculating  $R$ -factors(gt) *etc.*, and was not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  were statistically about twice as large as those based on  $F$ , and  $R$ -factors based on all data were even larger.

### Synthesis of [Sn<sub>2</sub>(pydcH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>O]<sub>n</sub>, 1

To a solution of 0.22 mmol (36 mg) of pyridine-2,6-dicarboxylic acid and 0.64 mmol (100 mg) of 4,4'-bipyridine in 20 ml water stirred for 1 h, was added an aqueous solution of 0.11 mmol (24 mg) tin(II) chloride dihydrate (10 ml). The molar ratio of the reaction shown in Scheme 1 was 6:2:1 for amine:acid:metallic salt. The resulting solution was heated to 60 °C and stirred for 30 min. In the final yellow solution, colorless crystals were obtained at room temperature after three weeks.

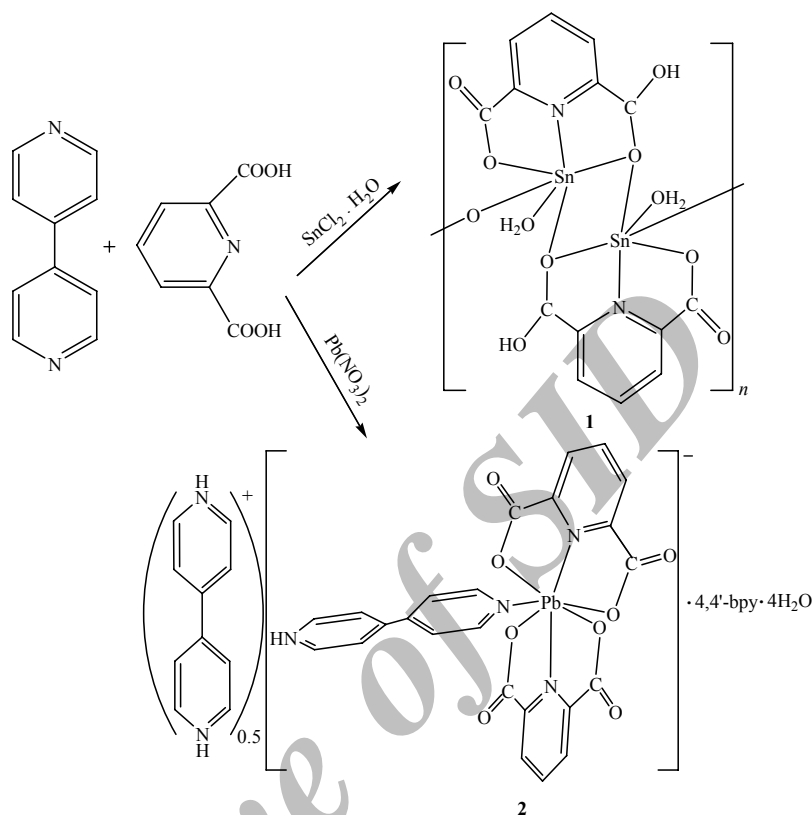
### Synthesis of (4,4'-bpyH<sub>2</sub>)<sub>0.5</sub>[Pb(pydc)<sub>2</sub>(4,4'-bpyH)].4,4'-bpy.4H<sub>2</sub>O, 2

To a solution of 0.22 mmol (36 mg) of pyridine-2,6-dicarboxylic acid and 0.64 mmol (100 mg) of 4,4'-bipyridine in 20 ml water stirred for 1 h, a 10 ml aqueous colorless solution of 0.11 mmol (35 mg) lead(II) nitrate was added (Scheme 1). The molar ratio of the reaction shown in Scheme 1 was 6:2:1 for amine:acid:metallic salt. The resulting solution was heated to 60 °C and stirred for 30 min. The final solution was filtered and after 10 days, colorless crystals were obtained in room temperature.

### Potentiometric pH Titrations

All potentiometric  $pH$  measurements were made on

## Two Novel Metal Organic Frameworks of Sn(II) and Pb(II)



Scheme 1

solutions in a 50 ml double-walled glass vessel using a Model 686 Metrohm Titroprocessor equipped with a combined glass-calomel electrode. The temperature was controlled at  $25.0 \pm 0.1$  °C by circulating water through the jacket, from a constant-temperature bath (MLW thermostat). The cell was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and a 10.00-ml capacity Metrohm piston burette were inserted and sealed with clamps and O-rings. Atmospheric  $\text{CO}_2$  was excluded from the titration cell with a purging stream of purified nitrogen gas. The  $\text{pH}$  meter-electrode system was calibrated to read  $-\log [\text{H}^+]$ .

The concentrations of bpy and  $\text{H}_2\text{pydc}$  were  $2.5 \times 10^{-3}$  M, for the potentiometric  $\text{pH}$  titrations in the presence and absence of  $8 \times 10^{-4}$  M  $\text{Sn}^{2+}$  and  $\text{Pb}^{2+}$ , and a standard carbonate-free NaOH solution (0.099 M) was used in all titrations. The ionic strength was adjusted to 0.1 M with KCl. The electrodes were calibrated in the thermostated cell with standard acid-base to read  $\text{pH}$  directly. The value of  $\text{p}K_{\text{W}} = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$  used in the calculations was  $10^{-13.78}$  [13]. Ionic strength was

adjusted to 0.1 M with KCl. Before an experimental point ( $\text{pH}$ ) was measured, sufficient time was allowed for establishment of equilibrium. Ligands protonation constants and their metal complexes protonation, stability and hydrolysis constants were calculated using the program BEST described by Martell and Motekaitis [14].

## RESULTS AND DISCUSSION

Our team has previously worked on structures similar to the title compounds, including  $(4,4'\text{-bpyH})_2[\text{Sb}(\text{pydc})(\text{OH})_2(\mu\text{-OH})_2 \cdot 8\text{H}_2\text{O}]$  [15],  $(4,4'\text{-bpyH})[\text{Cr}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}$  [16],  $(4,4'\text{-bpyH})_2[\text{Sr}(\text{pydc})_2(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$  [17],  $(2,2'\text{-bpyH})[\text{Al}(\text{pydc})_2] \cdot 3\text{H}_2\text{O}$  [18]. There are some other cases like  $\{[\text{Cd}(\text{py-2,4-dc})(2,2'\text{-bpy})] \cdot \text{H}_2\text{O}\}_n$ , py-2,4-dc: pyridine-2,4-dicarboxylate and 2,2'-bpy: 2,2'-bipyridine [19],  $[\text{Zn}_2(\text{py-2,4-dc})_2(4,4'\text{-bpy})(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$  [20] which are also similar to the title compounds. As can be seen, in the first four examples, 2,2'- or 4,4'-bpy acts as counter ion and is not coordinated to the

metal center. However, in the last two examples, 2,2'- or 4,4'-bpy is directly coordinated to the metal center. Also, as mentioned above, there are two instances with no bipyridine in the structure [8,9].

### X-Ray Crystallographic Study of 1

The crystallographic data, selected bond lengths, bond

angles, torsion angles and selected hydrogen bond geometries of  $[\text{Sn}_2(\text{pydcH})_2(\text{H}_2\text{O})_2\text{O}]_n$ , **1** are listed in Tables 1-3, respectively. The molecular structure of monomer, a part of the polymeric structure, coordination polyhedron and C-O $\cdots\pi$  interactions of **1** are illustrated in Figs. 1-4, respectively.

As shown in Fig. 1, in the monomeric structure of **1**, each Sn(II) atom is coordinated by a (pydcH)<sup>-</sup> group, a water

**Table 1.** Crystallographic Data

	Sn(II) compound, 1	Pb(II) compound, 2
Empirical formula	$\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_{11}\text{Sn}_2$	$\text{C}_{39}\text{H}_{36}\text{N}_7\text{O}_{12}\text{Pb}$
Formula weight	621.64	1001.95
Temperature (K)	150(2)	423(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)$ $Z = 2$	$P\bar{1}$ $Z = 2$
Unit cell dimensions	$a = 5.2456$ (3) Å $b = 11.1651$ (6) Å $c = 14.3230$ (7) Å $\beta = 97.415$ (2)°	$a = 8.1472$ (9) Å $b = 12.741$ (1) Å $c = 19.145$ (2) Å $\alpha = 106.513$ (2)° $\beta = 97.698$ (2)° $\gamma = 93.476$ (2)°
Absorption coefficient ( $\text{mm}^{-1}$ )	3.07	4.57
Min. and max. transmission factor	0.449, 0.749	0.244, 0.447
$F(000)$	596	994
Theta range for data collection	2.32 to 31.05°	2.27 to 28.52°
Index ranges	$-7 \leq h \leq 7$ , $-15 \leq k \leq 15$ , $-20 \leq l \leq 20$	$-9 \leq h \leq 9$ , $-15 \leq k \leq 15$ , $-22 \leq l \leq 22$
Reflections collected	20324	18302
Completeness to theta	99.9% (to $\theta = 31.05^\circ$ )	99.8% (to $\theta = 28.52^\circ$ )
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2660/1/264	6618/0/532
Goodness-of-fit on $F^2$	1.04	0.98
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0142$ , $wR2 = 0.0361$	$R1 = 0.0275$ , $wR2 = 0.0657$
Largest diff. peak and hole	0.55 and -0.81 e.Å <sup>-3</sup>	1.33 and -1.27 e.Å <sup>-3</sup>

Crystallographic data for the two structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 726575 for Sn(II) compound and CCDC 726576 for Pb(II) compound. 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).

**Table 2.** Selected Bond Lengths, Bond Angles and Torsion Angles

Compound 1			
Sn1-N2	2.260 (4)	Sn2-N1	2.257 (4)
Sn1-O5	2.391 (3)	Sn2-O1	2.371 (3)
Sn1-O8	2.190 (3)	Sn2-O4	2.202 (3)
Sn1-O10	2.502 (4)	Sn2-O9	2.492 (4)
Sn1-O11	1.889 (2)	Sn2-O11	1.896 (2)
C1-O1	1.283 (5)	C8-O5	1.280 (5)
C1-O2	1.241 (5)	C8-O6	1.230 (5)
N2-Sn1-O5	68.86 (12)	N1-Sn2-O1	68.61 (12)
N2-Sn1-O8	71.53 (12)	N1-Sn2-O4	71.70 (12)
N2-Sn1-O10	145.24 (12)	N1-Sn2-O9	144.26 (12)
N2-Sn1-O11	88.72 (17)	N1-Sn2-O11	87.67 (17)
O5-Sn1-O8	140.34 (12)	O1-Sn2-O4	140.17 (12)
O5-Sn1-O10	143.47 (12)	O1-Sn2-O9	143.05 (12)
O5-Sn1-O11	87.73 (12)	O1-Sn2-O11	85.10 (12)
O10-Sn1-O11	82.26 (17)	O4-Sn2-O9	74.37 (12)
O8-Sn1-O10	74.89 (12)	O4-Sn2-O11	90.25 (11)
O8-Sn1-O11	89.63 (11)	O9-Sn2-O11	81.55 (17)
Sn1-O5-C8-O6	178.6 (3)	Sn2-O1-C1-O2	178.1 (3)
Sn1-O8-C14-O7	-173.3 (3)	Sn2-O4-C7-O3	172.7 (3)
Compound 2			
Pb1-O1	2.400 (3)	Pb1-N1	2.523 (3)
Pb1-O4	2.734 (3)	Pb1-N2	2.672 (3)
Pb1-O5	2.784 (3)	Pb1-N3	2.752 (3)
Pb1-O8	2.556 (2)		
O1-Pb1-O4	125.76 (9)	O5-Pb1-O8	122.03 (8)
O1-Pb1-O8	86.65 (9)	O5-Pb1-N1	142.37 (9)
O1-Pb1-N1	66.34 (9)	O5-Pb1-N2	59.37 (8)
O1-Pb1-N2	71.50 (9)	O8-Pb1-N1	68.34 (9)
O1-Pb1-N3	77.49 (9)	O8-Pb1-N2	62.70 (8)
O4-Pb1-O5	146.13 (8)	O8-Pb1-N3	145.12 (9)
O4-Pb1-O8	86.46 (8)	N1-Pb1-N2	115.60 (9)
O4-Pb1-N1	61.19 (9)	N1-Pb1-N3	76.84 (9)
O4-Pb1-N2	145.04 (8)	N2-Pb1-N3	136.44 (9)

**Table 3.** Hydrogen Bond Geometry

D-H...A	D...A	H...A	D-H	<D-H...A
<b>Compound 1</b>				
O9-H9B...O6 <sup>i</sup>	0.95	1.77	2.683 (5)	160
O9-H9A...O3 <sup>ii</sup>	0.95	1.88	2.812 (5)	167
O10-H10B...O2 <sup>iii</sup>	0.95	1.75	2.661 (5)	161
O10-H10A...O7 <sup>iv</sup>	0.95	1.83	2.766 (5)	168
O3-H3A...N1 <sup>iii</sup>	0.95	2.36	3.105 (4)	135
O7-H7A...N2 <sup>i</sup>	0.95	2.47	3.222 (4)	137
C12-H12...O8 <sup>v</sup>	0.95	2.52	3.396 (5)	153
C3-H3...O6 <sup>vi</sup>	0.95	2.46	3.261 (6)	142
C4-H4...O3 <sup>vii</sup>	0.95	2.39	3.164 (5)	139
C5-H5...O4 <sup>vii</sup>	0.95	2.50	3.377 (5)	153
C10-H10...O2 <sup>viii</sup>	0.95	2.46	3.254 (5)	141
C11-H11...O7 <sup>v</sup>	0.95	2.41	3.180 (6)	137
Symmetry codes: (i) $x-1, y, z$ ; (ii) $-x, y-1/2, -z+1$ ; (iii) $x+1, y, z$ ; (iv) $-x-1, y+1/2, -z+2$ ; (v) $-x-1, y-1/2, -z+2$ .				
<b>Compound 2</b>				
O1S-H1A...O2S <sup>i</sup>	0.95	1.80	2.739 (4)	169
O1S-H1B...O4S <sup>ii</sup>	0.95	1.98	2.896 (5)	160
O2S-H2A...O3	0.95	1.84	2.793 (4)	178
O2S-H2B...O6 <sup>iii</sup>	0.95	1.85	2.785 (4)	169
O3S-H3A...O6 <sup>iii</sup>	0.95	1.85	2.786 (4)	167
O3S-H3B...O3	0.95	1.79	2.730 (4)	170
O4S-H4A...O1	0.95	1.96	2.898 (4)	171
O4S-H4B...O3S <sup>iv</sup>	0.95	1.87	2.797 (5)	165
N4-H4C...O5 <sup>v</sup>	0.95	1.70	2.638 (4)	171
N7-H7A...O7 <sup>vi</sup>	0.95	1.61	2.555 (4)	175
C16-H16...N5 <sup>ii</sup>	0.93	2.48	3.399 (5)	172
C18-H18...N6 <sup>i</sup>	0.93	2.42	3.341 (5)	170
C24-H24...O2 <sup>ii</sup>	0.93	2.24	3.160 (5)	173
C26-H26...O1S	0.93	2.29	3.211 (5)	170

Symmetry codes: (i)  $-x, -y+1, -z+1$ ; (ii)  $-x+1, -y, -z+1$ ; (iii)  $x, y+1, z$ ; (iv)  $x, y-1, z$ ; (v)  $-x, -y, -z+1$ ; (vi)  $x, y, z+1$ .

molecule and a single oxygen atom. There are two types of Sn(II) atoms in the structure, named Sn1 and Sn2, so the bond lengths and angles around both of them are given in Table 2. It can be seen that Sn1, Sn2, O1 and O5 atoms form a four-membered ring. The O11 atom coordinated to both Sn(II) atoms, have a significant shorter Sn-O bond lengths (see Table 2). In effect, O11 atom is the propagating factor, resulting in a one dimensional polymeric structure, a part of which is given in Fig. 2.

There are four carboxylate groups around the metal center. Obviously, among C-O bonds of each carboxylate group the bond containing the coordinated oxygen atom is clearly longer than the other. For instance, comparing C1-O1 and C1-O2 in Table 2, shows that the former which contains coordinated O1 atom is longer.

The study of the coordination polyhedron around the Sn(II) atom of compound **1** shown in Fig. 3 reveals that interestingly all the coordinated atoms are forced into one side of Sn(II) with the other side left empty. This could be a result of stereochemically active lone pair on Sn(II) center. Since in

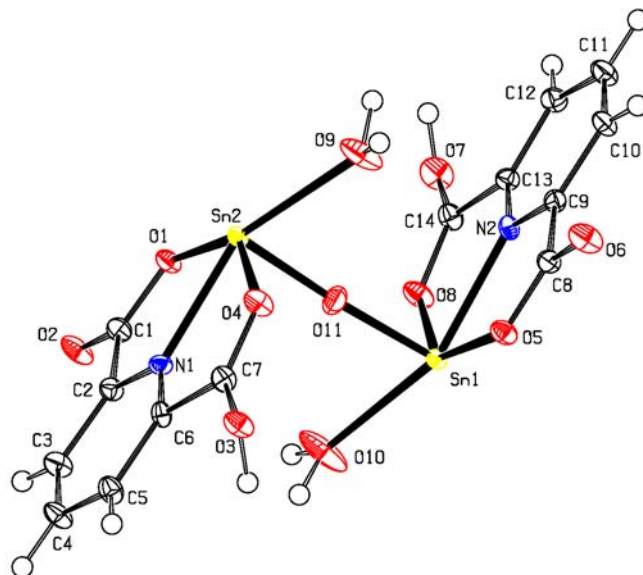


Fig. 1. Molecular structure of  $[\text{Sn}_2(\text{pydcH})_2(\text{H}_2\text{O})_2\text{O}]_n$ , **1**, shown in 50% probability.

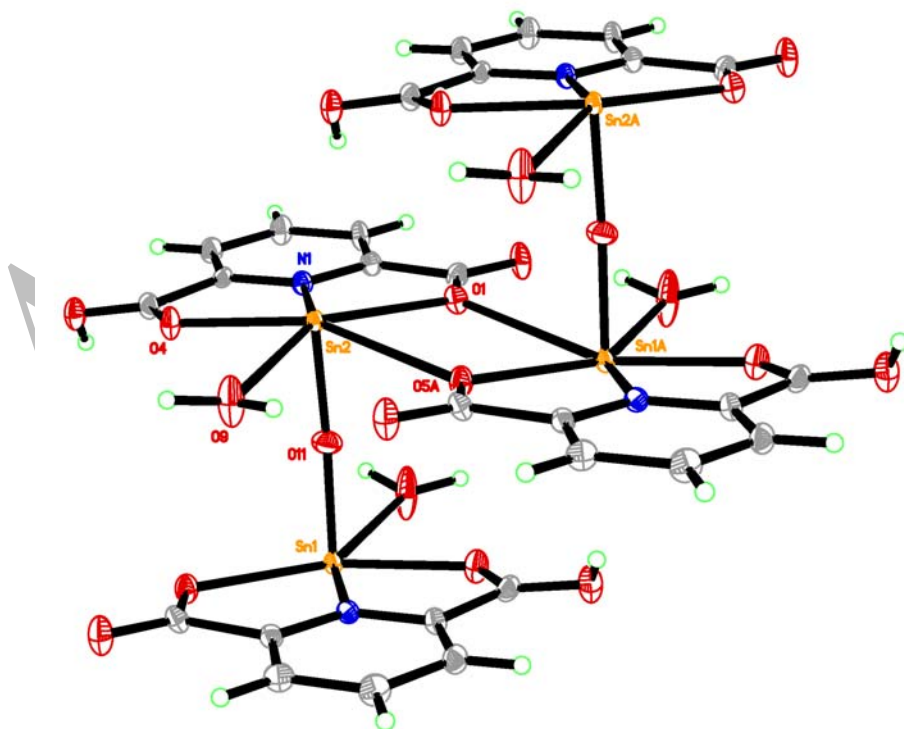


Fig. 2. A part of polymeric structure of **1**.

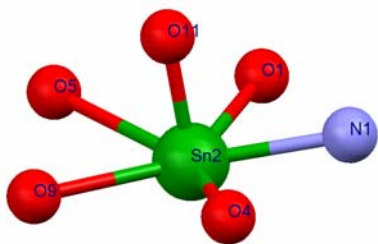


Fig. 3. Coordination polyhedron of **1**.

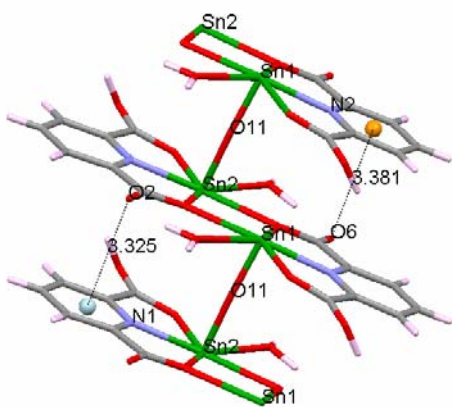


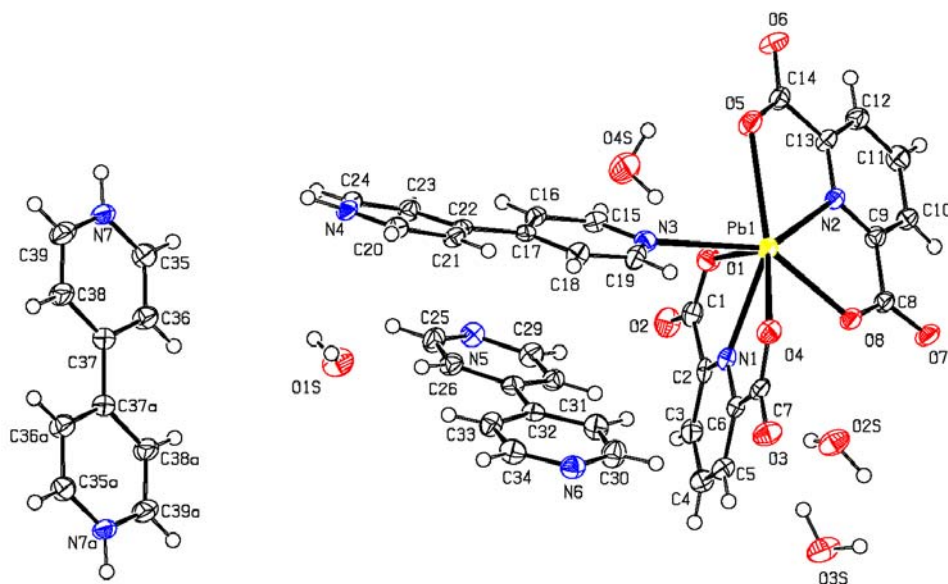
Fig. 4. The C-O... $\pi$  interactions between two parallel monomeric units of **1**, with the distances.

compound **1**, the Sn-O bond lengths are significantly different, it can be concluded that like Pb(II) complexes discussed in the following section, the active lone pair might be adjacent to the longer bonds resulting in a hemidirected geometry.

As shown in Table 3, various hydrogen bonds of type O-H...O, O-H...N and C-H...O are also responsible for the expansion of the structure. It is notable that the 1D ribbons are almost parallel to each other. Similarly, a ribbon, each monomeric unit is parallel to an adjacent unit so that there are two types of C-O... $\pi$  interactions between the uncoordinated O2 and O6 atoms of carboxylate groups and parallel aromatic rings ( $Cg_1$ : N1/C2-C6 and  $Cg_2$ : N2/C9-C13) of the adjacent monomers, shown in Fig. 4 with the distances of O2... $Cg_1$  3.324 (3) Å and O6... $Cg_2$  3.381 (3) Å, and angles of C1-O2... $Cg_1$  95.5 (2)° and C8-O6... $Cg_2$  91.2 (2)°, respectively. Consequently, it can be concluded that although the polymeric chain is propagated by Sn-O-Sn bond, the C-O... $\pi$  interactions help to hold the monomers together.

### X-Ray Crystallographic Study of **2**

The crystallographic data, selected bond lengths, bond angles and hydrogen bond geometries of (4,4'-bpyH<sub>2</sub>)<sub>0.5</sub>[Pb(pydc)<sub>2</sub>(4,4'-bpyH)].4,4'-bpy.4H<sub>2</sub>O, **2** are listed in Tables 1-3, respectively. The molecular structure, coordination polyhedron, all types of interactions and water cluster of **2** are illustrated in Figs. 5-8, respectively. As shown





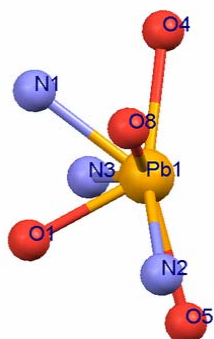


Fig. 6. Coordination polyhedron of **2**.

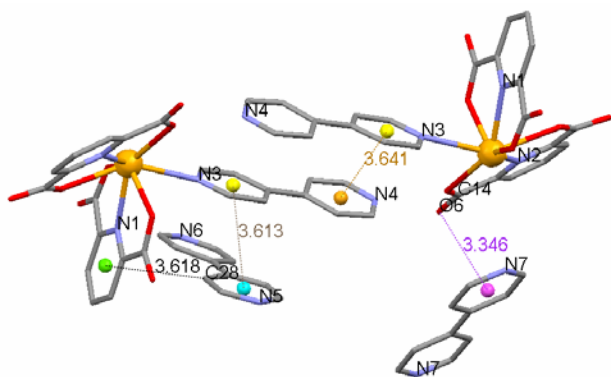


Fig. 7. The C-H... $\pi$ , C-O... $\pi$  and  $\pi$ ... $\pi$  interactions of **2**, hydrogen atoms are omitted for clarity.

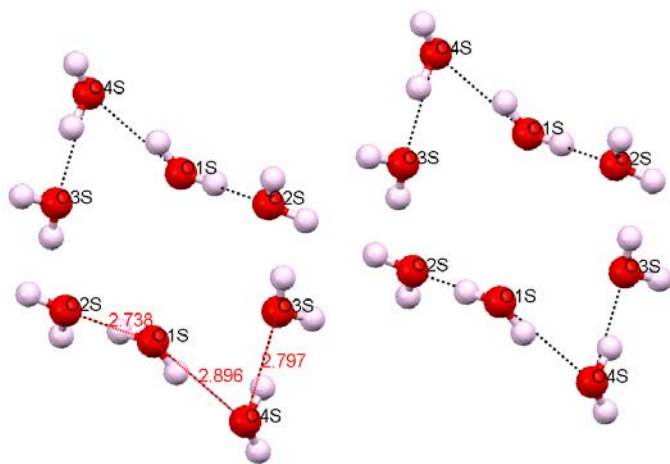


Fig. 8. Chain water clusters present in crystal lattice of **2**.

in Fig. 5, the Pb(II) atom is coordinated by two (pydcH)<sup>-</sup> groups and a (bpyH)<sup>2+</sup>, forming an anionic complex which is balanced by half a (bpyH<sub>2</sub>)<sup>2+</sup> group. In addition to mono and biprotonated forms of bipyridine, a neutral molecule of bipyridine is also present in the crystal lattice. Among the three bipyridines, the pyridine rings of the biprotonated form are almost coplanar.

Similar to compound **1**, a stereochemically active lone pair makes the bonds around Pb(II) atom locate on one side leaving an empty space (Fig. 6). There are some examples of the case, such as [Pb(2,2'-bpy)(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(bipd)(NO<sub>3</sub>)<sub>2</sub> and [Pb(Hpcih)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O) (2,2'-bpy = 2,2'-bipyridine, bipd = 1,4-bis(3-pyridyl)-2,3-diazo-1,3-butadiene, Hpcih = 2-pyridinecarbaldehyde isonicotinoylhydrazone) [21], [Sb(pydc)(H<sub>2</sub>O)]<sub>2</sub>O [22] and (tataH<sub>2</sub>)<sub>2</sub>[Pb(pydc)<sub>2</sub>]<sub>2</sub>·2tata·4H<sub>2</sub>O [23]. The Pb<sup>2+</sup> ion with the electronic configuration 4f<sup>14</sup>5d<sup>10</sup>6s<sup>2</sup> is a heavy *p*-block metal which possesses variable coordination behaviors caused by the stereochemically active lone pair. Its 6s electron pair, which may or may not play a role in the stereochemistry of lead(II) complexes, has recently been reviewed based on a crystal data available in the Cambridge Structure Database [24]. When the lone pair appears to have no steric effects, the bonds with ligand donor atoms are arranged throughout the surface of encompassing sphere (holodirected coordination) and all the Pb-L bonds are of intermediate length, and there are no marked differences in the Pb-L bond lengths. But Pb(II) complexes, in which the lone pair is stereochemically active, have 'hemidirected coordination', the Pb-L bonds are directed only to a part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand. There are the shorter Pb-L bonds away from the proposed site of the lone pair and the longer Pb-L bonds adjacent to this site of the lone pair [21]. Some bonds around Pb(II) as tabulated in Table 2, are obviously longer, for instance, Pb1-N2 and Pb1-N3 are significantly longer than Pb1-N1 or Pb1-O5 is obviously longer than other Pb-O (carboxyl O) bonds. Therefore, it can be concluded that the lone pair is present with a hemidirected geometry.

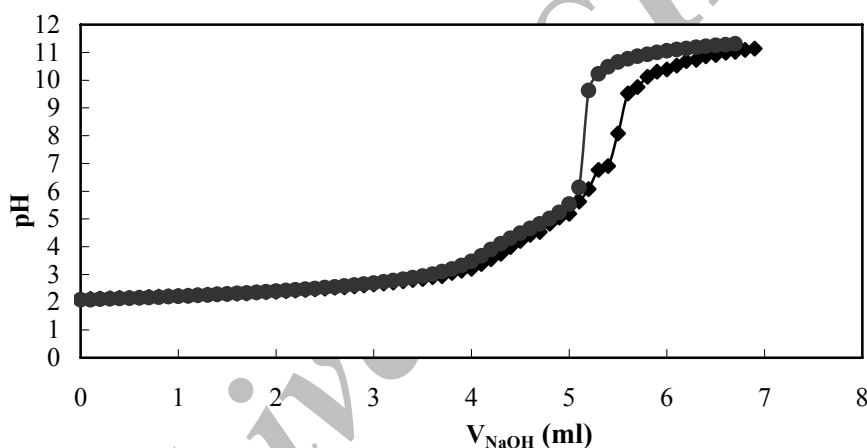
Various C-O... $\pi$ , C-H... $\pi$ ,  $\pi$ ... $\pi$  stackings and O-H...O, N-H...O, C-H...O and C-H...N hydrogen bonds are present in the lattice to stabilize the structure. The C-O... $\pi$  interactions can be observed with O6...Cg<sub>1</sub> 3.346(4) Å and C14-O6...Cg<sub>1</sub> 84.40°, Cg<sub>1</sub>: N7/C35-C39, C-H... $\pi$  with C28...Cg<sub>2</sub> 3.618(4) Å

and C28-H28...Cg<sub>2</sub> 155°, Cg<sub>2</sub>: N1/C2-C6,  $\pi$ ... $\pi$  stackings (with Cg<sub>3</sub>...Cg<sub>4</sub> distances of 3.613(2) and Cg<sub>3</sub>...Cg<sub>5</sub> distances of 3.641 (2) Å; Cg<sub>3</sub>: N3/C15-C19, Cg<sub>4</sub>: N5/C25-C29, Cg<sub>5</sub>: N4/C20-C24, all shown in Fig. 7. Uncoordinated water molecules of the lattice *i.e.* O1S, O2S, O3S and O4S form a four-membered chain water cluster with O...O bonds range of 2.739 (4) to 2.896 (5) Å (Fig. 8).

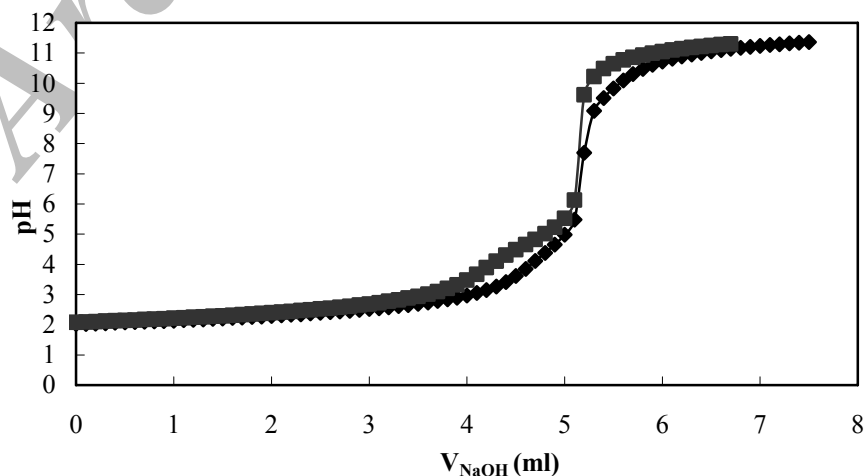
### Solution Studies

In order to evaluate the stoichiometry and stability of Sn<sup>2+</sup>

and Pb<sup>2+</sup> compounds with bpy and (pydc)<sup>2-</sup> in aqueous solutions, known concentrations of H<sub>2</sub>pydc, bpy and their 1:1 mixture in the absence and presence of the metal ions were titrated with a 0.099 M solution of NaOH at a temperature of 25 °C and an ionic strength of 0.1 M, maintained by KCl. The resulting pH profiles for Sn<sup>2+</sup> and Pb<sup>2+</sup> species are shown in Figs. 9 and 10, respectively. As can be seen, the potentiometric titration curves are depressed considerably in the presence of the metal ions clearly indicating their strong interactions with H<sub>2</sub>pydc.

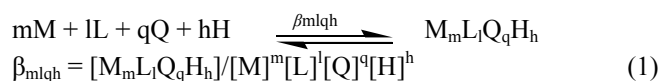


**Fig. 9.** Titration curve of ( $2.5 \times 10^{-3}$  M) pydc in absence and presence of ( $8 \times 10^{-4}$  M) Sn<sup>2+</sup> with experimental conditions of 25 °C, I = 0.1 M KCl: (●) pydc, (◆) pydc+Sn.



**Fig. 10.** Titration curve of ( $2.5 \times 10^{-3}$  M) pydc in absence and presence of ( $8 \times 10^{-4}$  M) Pb<sup>2+</sup> with experimental conditions of 25 °C, I = 0.1 M KCl: (■) pydc, (◆) pydc+Pb.

The extent of depression obviously depends both on the stoichiometries of the resulting complexes and the ability of the metal ions to bind the ligand components. The cumulative stability constants,  $\beta_{mlqh}$ , are defined by Eq. (1) (charges are omitted for simplicity)



where M is metal ion, L is pydc, Q is bpy and H is proton, and m, l, q, and h are the respective stoichiometric coefficients. Since the ligands' and complexes' activity coefficients are unknown, the  $\beta_{mlqh}$  values are defined in terms of concentrations. The errors are minimized by the use of a high-constant ionic strength of 0.1 M and low ligand concentrations (in the order of  $10^{-3}$  M).

The potentiometric pH titration curves of H<sub>2</sub>pydc, bpy and their 1:1 mixture in the presence of metal ions were fitted to the program BEST [14]. The resulting values for the most likely complexed species in aqueous solutions are listed in Table 4. Sample species distribution diagram for L+Q mixture in the absence and presence of Sn<sup>2+</sup> and Pb<sup>2+</sup> are also shown in

Figs. 11-13. The L, Q and their protonated forms are not shown in the distribution curves of metals for simplicity. The titration data of L+Q show that there is no detectable interaction (proton transfer) between L and Q. As it can be seen from Fig. 12 and Table 4, in the case of Sn<sup>2+</sup>, the most probable species are ML<sub>2</sub> and its hydroxide forms at higher pH values. The species ML<sub>2</sub>QH<sub>2</sub> is present at low pH. However, a complex with the stoichiometry similar to that obtained in the crystalline form was not found under solution study conditions.

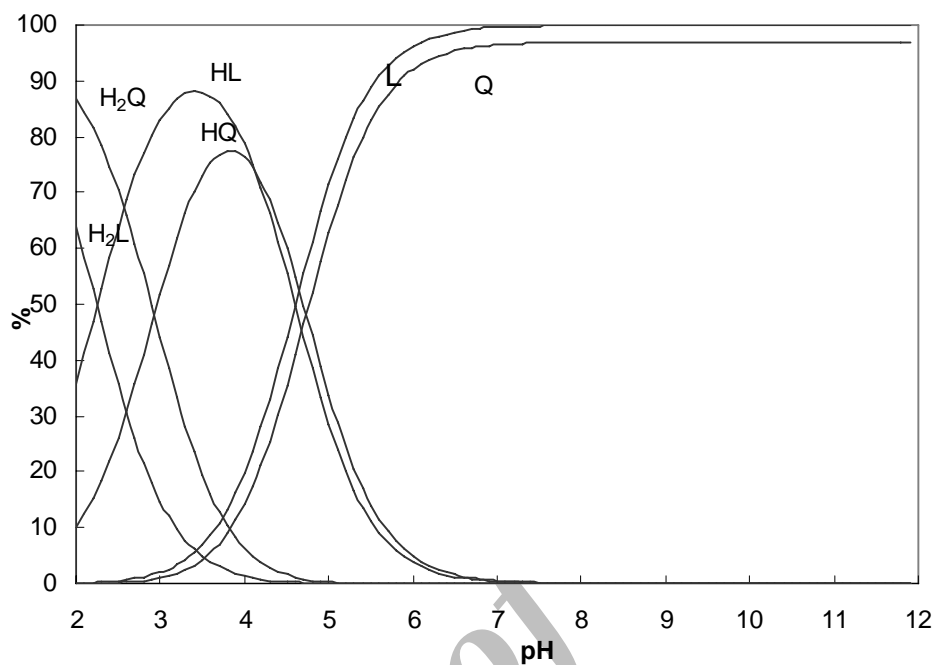
In the case of Pb<sup>2+</sup>, according to Fig. 13 and Table 4, the most abundant species in a wide range of pH is ML<sub>2</sub>, while ML and ML<sub>2</sub>OH exist only at low and high pH values, respectively. Species containing Q were not found in our solution studies, most probably due to the competition between K<sup>+</sup> ion and Q for neutralizing the ML<sub>2</sub> complex.

## CONCLUSIONS

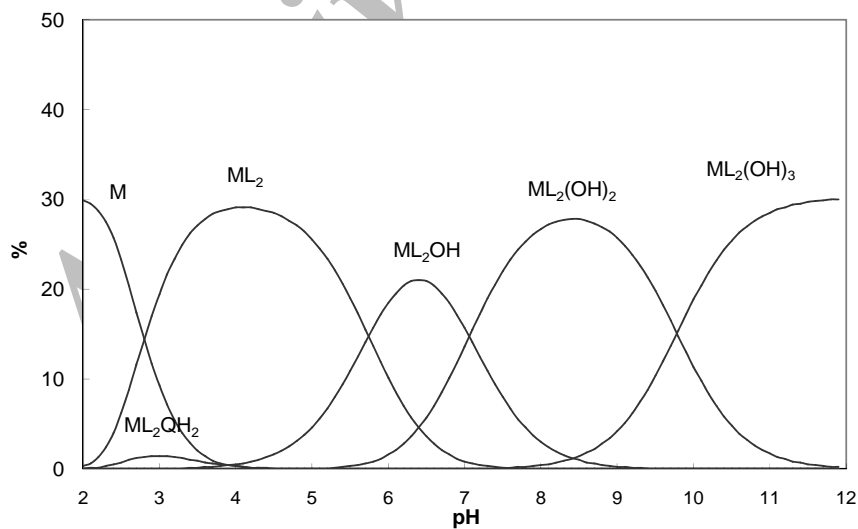
One would expect that the presence of acid and amine in the solution will result in a charged metallic complex balanced with a protonated amine as counter ion. However, in the crystal structure of some species like Sn(II) compound, **1**, the

**Table 4.** Overall Stability Constants for pydc<sup>2-</sup>(L), bpy (Q), Sn<sup>2+</sup> and Pb<sup>2+</sup> Compounds at 25 °C and I = 0.1 M KCl

L	Q	M	H	logβ	Max%	at pH
1	0	0	1	4.56	88.1	3.4
1	0	0	2	6.85	63.9	2.0
0	1	0	1	4.73	79.8	3.8
0	1	0	2	7.66	89.4	2.0
Sn <sup>2+</sup>						
2	0	1	0	9.35	29.1	4.1
2	0	1	-1	3.61	21.0	6.4
2	0	1	-2	-3.46	27.8	8.3
2	0	1	-3	-13.23	30.0	12.0
2	1	1	2	18.83	1.4	3.0
Pb <sup>2+</sup>						
1	0	1	0	10.08	33.9	2.0
2	0	1	0	14.20	31.6	5.7-6.7
2	0	1	-1	5.49	34.6	11.6-12.0



**Fig. 11.** Species distribution diagram for  $\text{pydc}^{2-}$  (L),  $\text{bpy}$  (Q) at 25 °C and ionic strength 0.1 M KCl.



**Fig. 12.** Species distribution diagram for  $\text{pydc}^{2-}$  (L),  $\text{bpy}$  (Q) and  $\text{Sn}^{2+}$  (M) at 25 °C and ionic strength 0.1 M KCl.

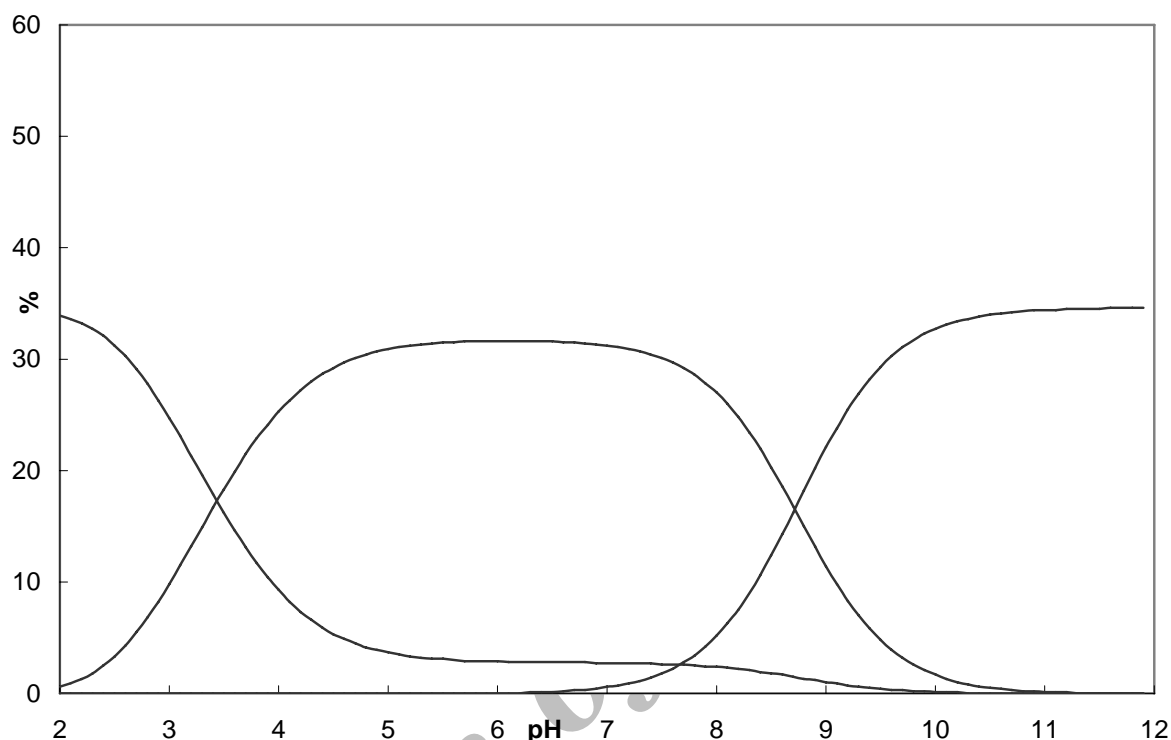


Fig. 13. Species distribution diagram for  $\text{pydc}^{2-}$  (L),  $\text{bpy}$  (Q) and  $\text{Pb}^{2+}$  (M) at 25 °C and ionic strength 0.1 M KCl.

complex is uncharged and the amine as a counter ion is absent. on the contrary, in the structure of Pb(II) compound, not only the anionic complex is balanced by biprotonated amine as counter ion, but also the monoprotinated form of amine is coordinated to the metal center, and also the neutral form of it, similar to water molecules is present in the crystal lattice. The most likely species detected in the solutioun studies were  $\text{ML}_2$ ,  $\text{ML}_2\text{OH}$ ,  $\text{ML}_2(\text{OH})_2$ ,  $\text{ML}_2(\text{OH})_3$  and  $\text{H}_2\text{ML}_2\text{Q}$ , in the case of  $\text{Sn}^{2+}$ , and  $\text{ML}$ ,  $\text{ML}_2$ , and  $\text{ML}_2\text{OH}$ , in the case of  $\text{Pb}^{2+}$  ion.

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