

## Supramolecular Structure of Calcium(II) Based on Chelidamic Acid: An Agreement Between Theoretical and Experimental Studies

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A novel supramolecular structure of an *s*-Block metal ion, Ca(II) atom, formulated as  $(\text{pnH}_2)_2[\text{Ca}_2(\text{H}_2\text{O})_2(\text{Hhpydc})_4]\cdot 4\text{H}_2\text{O}$  (**1**), was synthesized and characterized by elemental analysis, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and single crystal X-ray diffraction. Compound **1** is a member of a large family of supramolecular metallic compounds recently derived from a proton transfer ion pair,  $(\text{pnH}_2)(\text{Hhpydc})$ , where pn is propane-1,3-diamine and  $(\text{Hhpydc})^{2-}$  is 4-hydroxypyridine-2,6-dicarboxylate ion. Based upon the molecular structure analysis of the binuclear anionic complex, the coordination environment around each Ca(II) atom is pentagonal bipyramidal with seven-coordination number. The strong hydrogen bonding between hydroxyl groups of two neighboring anionic complexes produce the nice tape as X-like supramolecular structure. Optimization was carried out using two standard basis sets of 6-31G (d,p) for the single anionic complex (**S**) and LanL2MB basis set for the double anionic complexes (**D**) which describe the electrons of all atoms. As an interesting finding from our theoretical calculations, when we reoptimized the double complexes in the presence of strong hydrogen bond interaction between two hydroxyl groups, O3-H3A...O8<sup>ii</sup> (ii = x-1, y, z-1), it was revealed that the parallel position of ligands to each other was exactly like that of the solid state. The complexation reaction of H<sub>3</sub>hpydc with Ca<sup>2+</sup> in aqueous solution was investigated by potentiometric pH titrations, the equilibrium constants and species distribution in various pHs. The for major complexes formed are described.

**Keywords:** Calcium(II), Crystal structure, Hydrogen bonds, Coordination compounds, DFT, Solution studies

### INTRODUCTION

The coordination chemistry of groups IA and IIA metal compounds with organic ligands in the widest sense has been, until recently, largely unknown compared to transition metal coordination networks. This is true despite the fact that many *s*-Block metal-organic compounds are already of commercial

significance. Thus, pharmaceuticals, dyes and pigments typically use alkali and/or alkaline earth metal cations in preference to transition or lanthanide metal ions because most of them have the advantage of being non-toxic, cheap and soluble in aqueous media. Indeed, *s*-Block cations should not be ignored as simple "spectator" ions when it comes to properties which depend on the solid-state structure and the intermolecular interactions. This is especially true of pharmaceutical industry where one salt might be preferred

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over others for practical as well as commercial reasons. Therefore, understanding the changes in material properties caused by changing the *s*-Block metal ion depends on the consideration of the fundamental properties such as charge, size, and electronegativity of these cations and their influence on the nature of the resultant solid-state structure.

Furthermore, the chemistry of group IA and IIA metal ions is not limited to the classical ionic behavior as known from aqueous media, but may exhibit a more covalent character similar to transition metal compounds when polar organic solvents are used [1]. Self-assembly of molecular components gives rise to composite molecular aggregates with specific structures and activities, and is at the heart of various biological processes which are very sophisticated and complex. The first step in understanding these complicated processes is to unravel the interplay of non-covalent interactions (such as hydrogen bonding,  $\pi$ - $\pi$  stacking, C-H $\cdots$  $\pi$ , metal- $\pi$  interactions, *etc.*) that are responsible for crystal or solid formation [2-4]. Organic molecules, containing one or more carboxylic acid groups and/or other acidic groups, such as hydroxy derivatives of pyridine carboxylic acids, are able to coordinate to several metal centers in various modes and have been widely used for the synthesis of multi-dimensional coordination polymers.

Many transition metal complexes of these classes of ligands have extensively been investigated by our research group and others due to their great coordination potential as well as their biological significance [5-28]. Picolinic acids provide a very interesting model, as they are biologically important ligands incorporated into some enzymes whose molecule is an active agent in some drugs. The structures, chemical properties and biological activities of picolinic acid and some metal picolinate have been studied [29-31]. Picolinic acid is the body's prime natural chelator of vital trace elements such as chromium, zinc, manganese, copper, iron and molybdenum. Depending on the oxidation state of the metal, the coordination number and the kind of coordinated ligand, there are many structures of carboxylate, which show different biological and physico-chemical properties [32,33]. The literature shows that there is a direct relationship between the chemical structure and the antimicrobial properties of chemical compounds [34,35]. The dicarboxylic acids [HOOC-

X-COOH] (X = aliphatic or aromatic moiety) represent supramolecular connectors that can generate infinite high-dimensional networks as ion pairs through complementary hydrogen bonds involving a variety of basic building blocks such as amines, dipyridines and pyrazines whose analogues have been documented recently [36-38]. In our research group, several efforts are being made to design and synthesize such compounds with various ion pairs and metallic centers which recently have been reviewed [4].

Having synthesized (pnH<sub>2</sub>)(Hhpydc), (pnH<sub>2</sub>)<sub>2</sub>(btc).2H<sub>2</sub>O, (pnH<sub>2</sub>)(pydc).H<sub>2</sub>pydc.2H<sub>2</sub>O and (pnH<sub>2</sub>)(py-2,3-dc), where btc, pydc, H<sub>2</sub>pydc, py-2,3-dc are benzene-1,2,4,5-tetracarboxylic acid, pyridine-2,6-dicarboxylate, pyridine-2,6-dicarboxylic acid, and pyridine-2,3-dicarboxylic acid, respectively, and are proton transfer ion pairs, we synthesized an extended range of compounds applying the latter ion pairs and metallic salts such as Co(II) [39,40], Ni(II) [41], Cu(II) [40,42], Cd(II) [40], Hg(II) [43] and Ce(III) [44]. Our findings showed that the above-mentioned compounds were crystallized either as polymer or monomer none of which were isostructural with the reported binuclear structures in this paper. Applying our method to metallic complexes with such ion pairs, here, we intend to report the complexation of (pnH<sub>2</sub>)(Hhpydc) ion pair to Ca(II) atom as alkaline earth metal and then, analyze the molecular structure of the resulting *s*-Block metal coordination compound. Recently, our research group, at the Hartree-Fock (HF) and density functional (DF) levels of theory, has carried out the first-principle studies related to the above categories of coordination compounds [16]. We are primarily concerned with comparing the data obtained for the said inorganic complexes in the solid state and the theoretical calculations. Although the syntheses, structural and spectroscopic analyses and the development of such inorganic complex applications are extremely rich areas of research [4], relatively few high-level computational studies have been reported--implying the intensive computational demands imposed by the large size of some of these categories of species possessing dimer- and polymer-type supramolecular structures. We are reporting in this paper, the synthesis, characterization, crystal structure, theoretical and solution studies on binuclear structure of an *s*-Block metal coordination compound, *i.e.* (pnH<sub>2</sub>)<sub>2</sub>[Ca<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(Hhpydc)<sub>4</sub>]-4H<sub>2</sub>O, (1).

## EXPERIMENTAL

### Materials and Investigation Techniques

4-Hydroxypyridine-2,6-dicarboxylic acid (97%), propane-1,3-diamine (99%) and Ca(II) nitrate tetrahydrate (99.9%) were purchased from Merck chemicals and used without further purification. IR spectroscopy was performed applying a Perkin-Elmer 343 spectrophotometer ( $200\text{--}4000\text{ cm}^{-1}$ ) using KBr discs. NMR spectra were recorded on a Bruker DRX 500-Avance spectrometer. Chemical shifts are reported on the  $\delta$  scale relative to TMS. Elemental analysis was performed on a Perkin-Elmer 2004(II). The X-ray data were obtained with a Bruker SMART Diffractometer. The melting point was determined applying a Barnstead Electrothermal 9200 apparatus.

### Potentiometric pH Titrations

All potentiometric pH measurements were made on 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  $25.0 \pm 0.1\text{ }^\circ\text{C}$  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 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 concentrations of pn and  $\text{H}_3\text{hypydc}$  were  $2.5 \times 10^{-3}\text{ M}$ , for the potentiometric pH titrations in presence and absence of  $8.0 \times 10^{-4}\text{ M Ca}^{2+}$ . Standard carbonate-free NaOH solution (0.092 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 pH directly. The value of  $pK_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$  used in the calculations was  $10^{-13.78}$  [45]. Ionic strength was adjusted to 0.1 M with KCl. Before an experimental point (pH) was measured, sufficient time was allowed for the 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* [46].

### Preparation of $(\text{pnH}_2)_2[\text{Ca}_2(\text{H}_2\text{O})_2(\text{Hhypydc})_4]\cdot 4\text{H}_2\text{O}$ (1)

An aqueous solution containing 0.2 mmol (47 mg) of  $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  in 10 ml water was mixed with 0.4 mmol (115 mg) of  $(\text{pnH}_2)(\text{Hhypydc})$  ion pair [47] (where  $(\text{pnH}_2)(\text{Hhypydc})$  ion pair as a proton transfer compound was prepared by the reaction of  $\text{H}_3\text{hypydc}$  with pn) in 30 ml  $\text{H}_2\text{O}$ . After 30 min stirring and heating to  $30\text{ }^\circ\text{C}$ , the solution was cleared. The total volume of the resulting solution was 60 ml which was allowed to stand for two weeks in the laboratory atmosphere. After that, colorless crystals in block type were obtained and selected for single crystal X-ray structure determination with the yield of 45% based on Ca. d.p.  $> 400\text{ }^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ )  $\delta$  (ppm): 7.00 (s, 4H, CH, 4Hhypydc), 1.93-3.05 (m, 6H,  $\text{CH}_2$ ,  $\text{pnH}_2$ );  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}$ )  $\delta$  (ppm): 24.3 (s,  $\text{pnH}_2$ ), 36.1 (s,  $\text{pnH}_2$ ), 116.2 (s, Hhypydc), 143.2 (s, Hhypydc), 165.4 (s, Hhypydc), 182.3 (s, Hhypydc). Anal. Calcd. for  $\text{C}_{34}\text{H}_{48}\text{N}_8\text{O}_{26}\text{Ca}_2$ : C, 38.34; H, 4.51; N, 10.52. Found: C, 38.04; H, 4.51; N, 10.54%. Selected IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3530-2526 (br, stretching CH, NH and OH), 1632 and 1385 (shoulder, m,  $\text{COO}^-$  group), 1580 (s, scissoring NH), 1576-1427 (m, aromatic C=C), 1170 (shoulder, stretching CN).

### X-Ray Crystallography

X-Ray structure analysis of prismatic colorless single crystals of  $(\text{pnH}_2)_2[\text{Ca}_2(\text{H}_2\text{O})_2(\text{Hhypydc})_4]\cdot 4\text{H}_2\text{O}$  was carried out on a Bruker SMART diffractometer with an APEX II CCD area detector (Mo- $\text{K}\alpha$  radiation, graphite monochromator,  $\lambda = 0.71073\text{ \AA}$ ). Diffracted data were corrected for absorption using the SADABS program [48,49]. Some software including APEX II (data collection), SAINT<sup>+</sup> (cell refinement and data reduction) and SHELXTL (version 6.2, structure solution & refinement; molecular graphics and publication material) were used [50,51].

## RESULTS AND DISCUSSION

### IR and NMR Spectral Characterization

The compound **1** was synthesized by the reaction of  $(\text{pnH}_2)(\text{Hhypydc})$  ion pair with Ca(II) nitrate salt in 2:1 molar ratio. Obviously, the observed shifts and splitting of the corresponding peaks compared to the free ion pair reveal

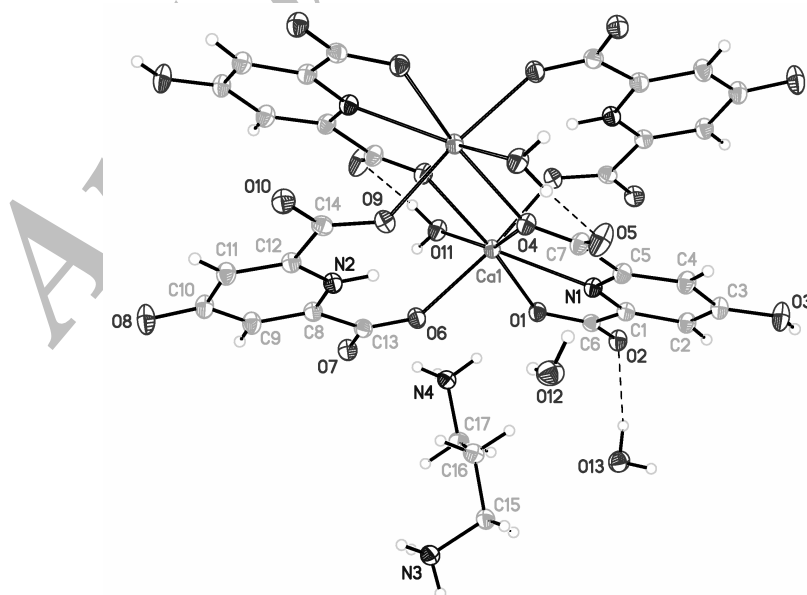
ligand coordination to the metal ion. The IR spectrum of the  $(\text{pnH}_2)_2[\text{Ca}_2(\text{H}_2\text{O})_2(\text{Hhpydc})_4]\cdot 4\text{H}_2\text{O}$ , was recorded in the 200-4000  $\text{cm}^{-1}$  region. The characteristic peaks of  $(\text{pnH}_2)(\text{Hhpydc})$  are observed as would be expected. For example, the peaks of 3530-2526  $\text{cm}^{-1}$  are attributed to stretching C-H, N-H and O-H bonds of  $(\text{pnH}_2)^{2+}$ ,  $(\text{Hhpydc})^{2-}$ , and crystallization waters of the lattice. Apparently, the peaks located at 1632 and 1385  $\text{cm}^{-1}$  are attributed to C=O and C-O bonds of carboxylate groups. These bands are related to those of 1610 and 1365  $\text{cm}^{-1}$  in the free ion pair attributed to the resonance of carboxylate group. Indeed,  $\nu(\text{C-O})$  and  $\nu(\text{C=O})$  bands are transformed into the symmetric and antisymmetric stretching vibrations of the carboxylate anion [31] that in the complex form lose such resonances because of the complex formation. The prominent band of 1580  $\text{cm}^{-1}$  is typical of scissoring NH vibration and the multiplet, medium peaks at 1576-1427  $\text{cm}^{-1}$  are due to aromatic C=C bonds. Finally, the featured 1170  $\text{cm}^{-1}$  is attributed to the stretching mode of C-N bonds.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1** show the expected peak resonances due to the proton and carbon atoms of  $(\text{pnH}_2)^{2+}$  and of  $(\text{Hhpydc})^{2-}$  moieties. The  $^1\text{H}$  NMR spectrum of the title

compound in  $\text{D}_2\text{O}$  solvent, showed the signal for the protons of the  $(\text{Hhpydc})^{2-}$  and  $(\text{pnH}_2)^{2+}$  groups at  $\delta = 1.93$ -3.05 and 7.00 ppm, respectively. The  $^{13}\text{C}$  NMR spectrum demonstrates six single features in the ranges of 24.34-36.09 and 116.19-182.27 ppm which verify the presence of  $(\text{pnH}_2)^{2+}$  and of  $(\text{Hhpydc})^{2-}$  moieties in the crystalline network. By comparing these data with those of the free  $(\text{pnH}_2)(\text{Hhpydc})$  ion pair, one can conclude that hydrogen-bonding interactions and complexation decrease the electron density around each proton and, thus, their chemical shifts are further toward the weak field.

### Crystal Structure Description

The adopted numbering scheme of the non-hydrogen atoms along with the thermal vibrational ellipsoids of the title compound are shown in Fig. 1. A summary of the parameters for the data collection and refinements for the title compound is given in Table 1. Selected bond distances, angles, and torsion angles are given in Table 2. In addition, a list of hydrogen bonds is given in Table 3. In the unit cell, the molecular structure of compound **1** contains the  $[\text{Ca}_2(\text{H}_2\text{O})_2(\text{Hhpydc})_4]^{2-}$  anion with propane-1,3-diamonium



**Fig. 1.** The adopted numbering scheme of the non-hydrogen atoms along with the thermal vibrational ellipsoids of the title compound.

**Table 1.** Crystal Data and Refinement Parameters for **1**

Empirical formula	C <sub>34</sub> H <sub>48</sub> Ca <sub>2</sub> N <sub>8</sub> O <sub>26</sub>
Formula weight	1064.96
Temperature (K)	100 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group, unit cell	<i>P</i> $\bar{1}$ (No. 2) <i>Z</i> = 1
Unit cell dimensions	<i>a</i> = 9.7866(4) Å <i>b</i> = 10.9870(4) Å <i>c</i> = 11.0757(4) Å $\alpha$ = 70.7580(10)° $\beta$ = 87.1230(10)° $\gamma$ = 87.4120(10)°
Unit cell volume (Å <sup>3</sup> )	1122.45(7)
Absorption coefficient (mm <sup>-1</sup> )	0.357
F(000)	556
Theta range for data collection	2.0 to 30.5°
Index range	-13 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 15 -15 ≤ <i>l</i> ≤ 15
Reflection collected	20069
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	6757/0/316
Goodness-of-fit on F <sup>2</sup>	1.022
Final <i>R</i> indices [ <i>I</i> > 2.0 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0270, <i>wR</i> 2 = 0.0758
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0285, <i>wR</i> 2 = 0.0771

organic moiety, and water molecules in a 1:2:4 molar ratio, respectively. Based upon the molecular structure analysis of the binuclear anionic complex, one finds that the coordination environment around Ca(II) atom is pentagonal bipyramidal (hereafter pbp) with seven-coordination number (Fig. 2). In fact, the O6-Ca1-O9<sup>i</sup> bond angle of 166.72 (2)° (*i* = 1-*x*, 1-*y*, 1-*z*), which is related to the axial position of pbp geometry, and the summation of O-Ca-O and O-Ca-N angles in the equatorial plane (360.38°), provide clear evidence for the proposed hypothesis. However, the axial angle is significantly different from the ideal value of 180° in pbp geometry which can be related to the steric effect of ligands in connection with

two Ca(II) atoms.

The two kinds of water molecules existing in the unit cell are the coordinated water molecule which occupies the equatorial position in the anionic complex and free water molecules that form the water dimer with D...A, H...A distances and D-H...A angle, 2.737, 1.937 Å, and 168.43°, respectively. Since the two hydrogen atoms of the coordinated water molecule (H11A and H11B) are engaged in the strong hydrogen bonding with oxygen atoms of carboxylate groups (O5 and O2) as an intra- and inter-molecular interactions, respectively, the basicity of the oxygen atom of the water molecule can be increased and therefore, the bond length of

**Table 2.** Selected Bond Distances, Bond Angles, and Torsion Angles for **1**

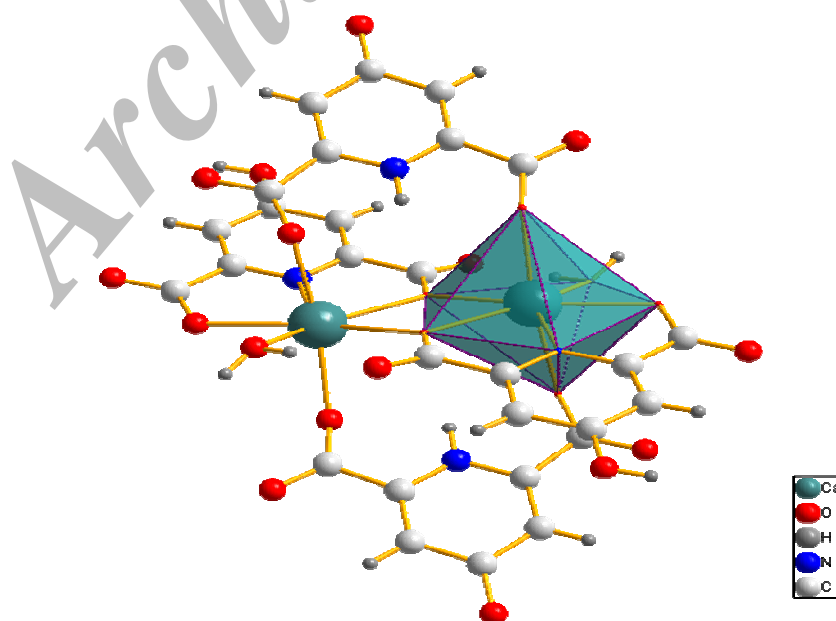
Ca1-O6	2.3177(6)	O4-C7	1.2742(10)
Ca1-O9 <sup>i</sup>	2.3302(6)	O5-C7	1.2464(10)
Ca1-O11	2.3827(6)	O6-C13	1.2577(9)
Ca1-O1	2.4256(6)	O7-C13	1.2518(10)
Ca1-O4 <sup>i</sup>	2.4356(6)	O8-C10	1.2740(10)
Ca1-N1	2.4617(7)	O9-C14	1.2606(10)
Ca1-O4	2.5167(6)	O10-C14	1.2447(10)
O1-C6	1.2697(9)		
O2-C6	1.2522(9)		
O3-C3	1.3345(9)		
O6-Ca1-O9 <sup>i</sup>	166.72(2)	O6-Ca1-N1	111.15(2)
O6-Ca1-O11	85.31(2)	O9 <sup>i</sup> -Ca1-N1	79.23(2)
O9 <sup>i</sup> -Ca1-O11	81.41(2)	O11-Ca1-N1	139.62(2)
O6-Ca1-O1	93.48(2)	O1-Ca1-N1	65.05(2)
O9 <sup>i</sup> -Ca1-O1	83.31(2)	O4 <sup>i</sup> -Ca1-N1	132.66(2)
O11-Ca1-O1	77.78(2)	O6-Ca1-O4	97.86(2)
O6-Ca1-O4 <sup>i</sup>	84.98(2)	O9 <sup>i</sup> -Ca1-O4	94.14(2)
O9 <sup>i</sup> -Ca1-O4 <sup>i</sup>	93.93(2)	O11-Ca1-O4	152.45(2)
O11-Ca1-O4 <sup>i</sup>	83.58(2)	O1-Ca1-O4	128.96(2)
O1-Ca1-O4 <sup>i</sup>	161.36(2)	O4 <sup>i</sup> -Ca1-O4	69.54(2)
C9-C8-C13-O7	4.27(12)	C4-C5-C7-O4	163.75(8)
C9-C8-C13-O6	-175.07(8)	C4-C5-C7-O5	-15.67(12)
C2-C1-C6-O1	179.08(7)	C11-C12-C14-O10	-2.03(12)
C2-C1-C6-O2	-2.09(11)	C11-C12-C14-O9	178.22(8)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ .

**Table 3.** The Geometry of Intra- and Inter-Molecular Interactions in **1**

D-H...A	D-H	H...A	D...A	D-H...A
O3-H3A...O8 <sup>ii</sup>	0.86	1.71	2.5659(10)	178
N3-H3B...O12 <sup>iii</sup>	0.89	1.88	2.7451(10)	164
N3-H3C...O10 <sup>iv</sup>	0.94	1.99	2.8720(10)	156
N3-H3D...O7 <sup>v</sup>	0.91	1.96	2.8459(10)	165
N4-H4B...O1	0.88	1.95	2.8162(9)	166
N4-H4C...O9 <sup>vi</sup>	0.89	2.51	3.2471(10)	141
N4-H4C...O10 <sup>vi</sup>	0.89	2.41	3.0326(10)	127
N4-H4C...O1 <sup>vii</sup>	0.89	2.35	3.0024(9)	131
N4-H4D...O7	0.88	2.02	2.8901(10)	170
O11-H11A...O5 <sup>i</sup>	0.86	1.81	2.6518(10)	165
O11-H11B...O2 <sup>vii</sup>	0.86	1.90	2.7386(10)	166
O12-H12A...O13 <sup>viii</sup>	0.81	1.94	2.7373(10)	168
O12-H12B...O8 <sup>iv</sup>	0.83	1.95	2.7419(10)	161
O13-H13A...O2	0.87	2.02	2.8768(9)	165
O13-H13B...O5 <sup>ix</sup>	0.84	1.96	2.7971(9)	176

Symmetry codes: (ii)  $x-1, y, z-1$ ; (iii)  $-x+2, -y+1, -z$ ; (iv)  $-x+2, -y+1, -z+1$ ; (v)  $-x+2, -y, -z+1$ ; (vi)  $x, y-1, z$ ; (vii)  $-x+1, -y, -z+1$ ; (i)  $-x+1, -y+1, -z+1$ ; (viii)  $x, y+1, z$ ; (ix)  $-x+1, -y+1, -z$ .



**Fig. 2.** Representation of the coordination environment around  $\text{Ca}^{2+}$  as pentagonal bipyramidal with seven-coordination number.

Ca-O11 is shorter than the other equatorial bond lengths. It is interesting to note that the intera-molecular proton transferring between hydroxyl group and pyridine ring of (Hhpydc)<sup>2-</sup> ligand leads to the protonation of pyridine nitrogen atom, hence conversion of hydroxyl group to C=O group. Based on this evidence, the strong hydrogen bonding between hydroxyl groups of the neighboring anionic complex and the C=O occurs with D...A, H...A distances and D-H...A angle, 2.5659(10), 1.705 Å, and 178.13°, respectively, and therefore, produce the nice tape-like supramolecular structure (Fig. 3). In addition, the  $\pi$ - $\pi$  stacking interactions between the pyridine ring systems can affect the creation of the tape-like structure. Finally, the presence of strong hydrogen bonding of the coordinated water molecule and carboxylate group, O11-H11B...O2, which are shown in Fig. 3, make the close distance between the tapes of each complex. Indeed, these van der Waals interactions form the unique supramolecular network in the crystal structure whose organic cationic moieties and water molecules fill the spaces between these tape-like structures.

### Theoretical Studies

Density functional (DF) calculations were done with Gaussian 98 program. The DFT level calculations were made with Beck's three parameter hybrid functional using the Lee-Yang-Parr correlation functional (B3LYP) [52-54]. Optimization was done using two standard basis set of 6-31G (d,p) for the single anionic complex (**S**) and LanL2MB basis set for the double anionic complexes (**D**) which describe the electrons of all atoms. According to the density functional theory (DFT), a study of single ionic complex revealed that the obtained optimized complex was theoretically different from the complex obtained by single crystal X-ray structure determination. Indeed, during the optimization process the coordinated ligands were completely changed from parallel into perpendicular state (Fig. 4a).

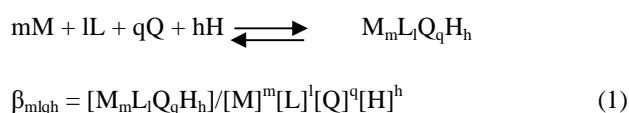
As an interesting finding from our theoretical calculations, when we reoptimized the double complexes in the presence of strong hydrogen bond interaction between two hydroxyl groups, O3-H3A...O8<sup>ii</sup> (ii = x-1, y, z-1), it was revealed that the parallel position of ligands to each other was exactly like that of the solid state (Fig. 4b,c). As a true evidence, the distance between the oxygen atoms of hydroxyl group in the inside part, 6.46 Å, was closer to the experimental value, 5.15

Å, than in the outside part (9.35 Å). This observation reveals that O3-H3A...O8<sup>ii</sup> interaction can play essential role in the geometrical properties of the title complex and also, in the construction of the special arrangement of crystalline network as a tape-like structure. Geometrical parameters of the optimized structures obtained by DFT quantum chemical calculations together with the corresponding experimental values are reported in Table 4. These results indicate that the agreement between the theoretical data and the experimental values is good in the inside part of the double complexes.

### Solution Studies

In order to evaluate the stoichiometry and stability of Ca<sup>2+</sup> complexes with H<sub>3</sub>hpydc in aqueous solution, known concentrations of pn and H<sub>3</sub>hpydc and their 1:1 mixture in the absence and presence of the metal ions were titrated with a 0.092 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 are shown in Fig. 5. It was found that H<sub>3</sub>hpydc had good interaction with metal ions, because the potentiometric titration curves were depressed considerably in the presence of the metal ions. The extent of the depression obviously depends on both the stoichiometries of the resulting complexes and the ability of the metal ions to bind the ligand components.

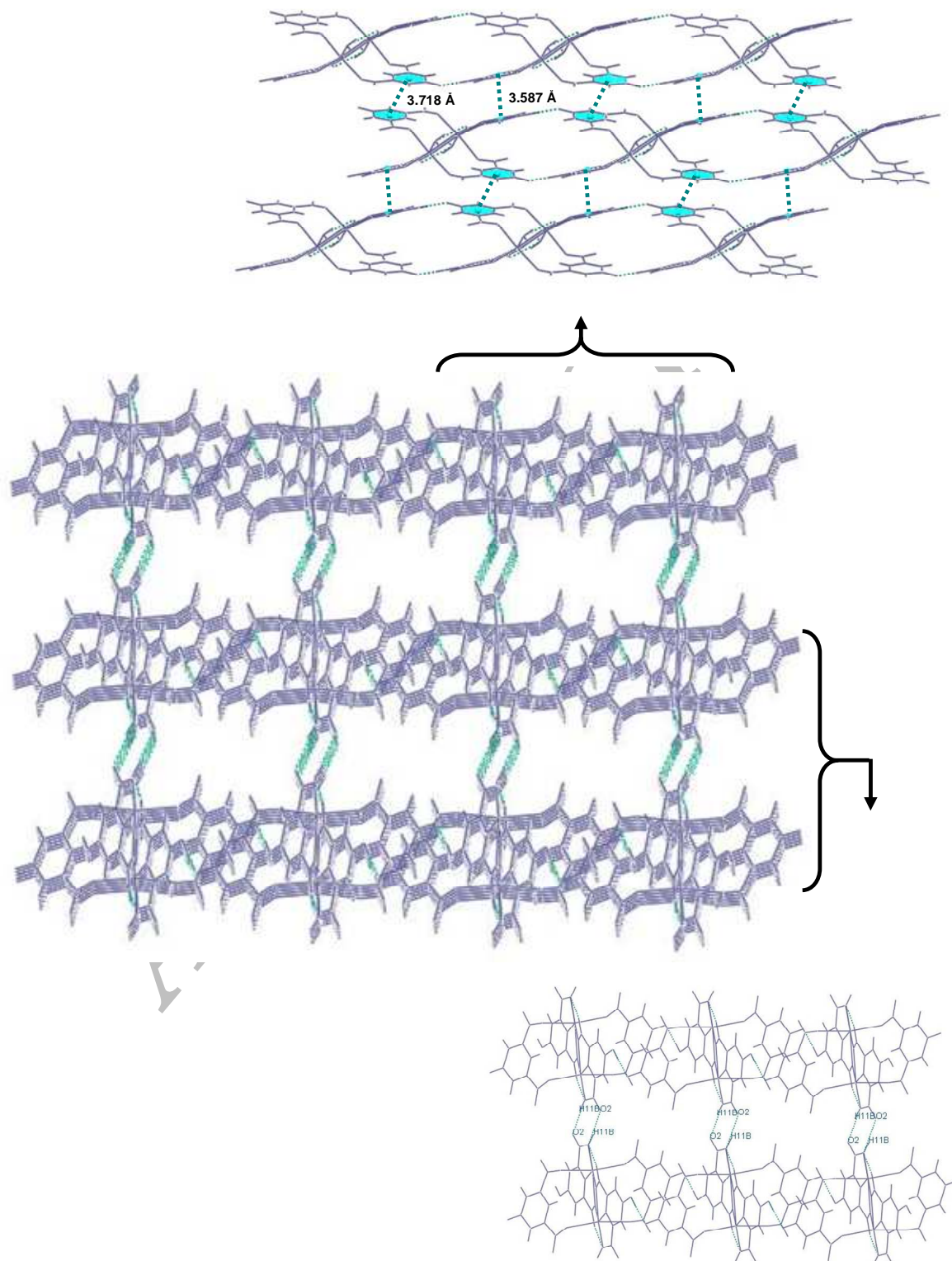
The cumulative stability constants,  $\beta_{mlqh}$ , are defined by Eq. (1) (charges are omitted for simplicity)



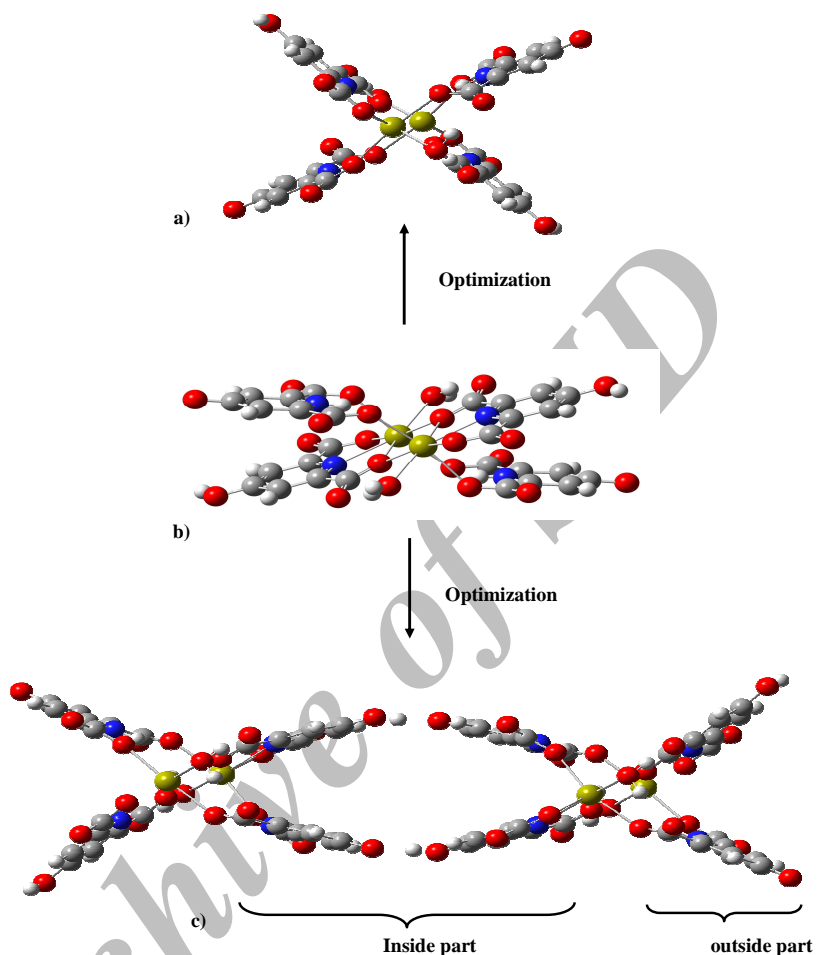
where M is the metal ion, L is (hpydc)<sup>3-</sup>, Q is (pnH<sub>2</sub>)<sup>2+</sup>, H is the proton, and m, l, q and h are the respective stoichiometric coefficients. Since the ligands' and complexes activity coefficients are unknown, the  $\beta_{mlqh}$  values are defined in terms of concentrations. 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<sup>-3</sup> M). The potentiometric pH titration curves of H<sub>3</sub>hpydc, pn and their 1:1 mixture in the presence of metal ions were fitted to the program BEST and the resulting values for the most likely complexed species in aqueous solutions are listed in Table 5. Sample species distribution diagram for Q and L + M, shown in Figs. 6 and 7,



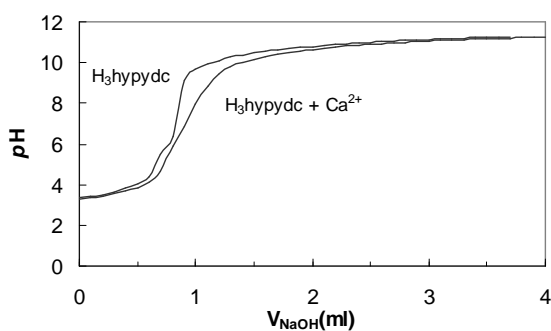
Supramolecular Structure of Calcium(II) Based on Chelidamic Acid



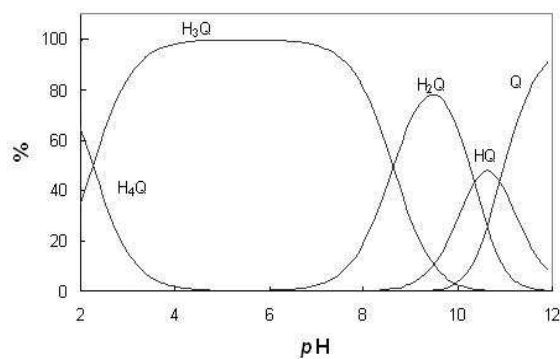
**Fig. 3.** The tape-like supramolecular structure of anionic complex *via*  $\pi$ - $\pi$  stacking interactions between two pyridine rings along with strong hydrogen bonding between coordinated water molecule and carboxylate group.



**Fig. 4.** Representation of b) initial, optimized a) single and c) double complexes of anionic Ca(II) complex.



**Fig. 5.** Titration curve of ( $2.5 \times 10^{-3}$  M)  $\text{H}_3\text{hypycd}$  in absence and presence of ( $8.0 \times 10^{-4}$  M)  $\text{Ca}^{2+}$  with experimental conditions of  $25^\circ\text{C}$ ,  $I = 0.1$  M (KCl).



**Fig. 6.** Species distribution diagram for  $\text{pH}_2$  (Q) at  $25^\circ\text{C}$  and ionic strength 0.1 M KCl.

Supramolecular Structure of Calcium(II) Based on Chelidamic Acid

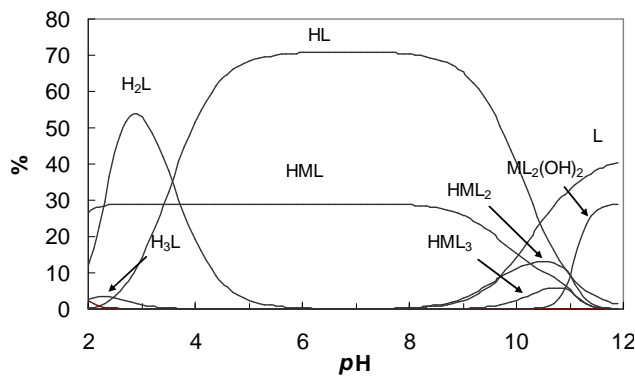
**Table 4.** Geometrical Parameters of Calculated Structures of Single Complex (S) and in Inside and Outside Parts of Double Complexes (D) at the B3LYP/6-31G (d, p) and B3LYP/LanL2MB Levels, Respectively, with Experimental Values from X-Ray Analysis (Distances in Å, Angles in °)

Geometrical parameters	B3LYP			Exp.*
	S	D Inside	D Outside	
Ca1-O6	2.39	2.41	2.40	2.32
Ca1-O9	2.36	2.39	2.45	2.33
Ca1-O1	2.47	2.45	2.57	2.43
Ca1-O11	2.50	2.45	2.49	2.38
Ca1-N1	2.62	2.57	2.65	2.46
Ca-O4 <sup>i</sup>	2.58	2.60	2.70	2.43
Ca...Ca	4.54	4.50	4.50	4.07
O-H(hydroxyl group)	0.97	1.02	0.98	0.86
C-O(hydroxyl group)	1.38	1.36	1.41	1.33
O6-Ca-O9 <sup>i</sup>	170.3	162.7	175.8	166.7
O11-Ca-O1	85.3	88.4	85.7	77.8
O1-Ca-N1	64.2	64.3	62.6	65.1
N1-Ca-O4	60.2	62.3	61.1	64.4
O4-Ca-O4 <sup>i</sup>	65.4	67.1	65.9	69.5

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ .

**Table 5.** Overall Stability Constants for H<sub>3</sub>hypdc (L) and Ca<sup>2+</sup> (M) Complexes at 25 °C and I = 0.1 M KCl

M	L	H	Q	logβ	Max%	at pH
0	1	1	0	10.45	70.8	6.5-7.1
0	1	2	0	14.02	53.7	2.9
0	1	3	0	15.39	3.4	2.4
0	0	1	1	10.83	48	10.6
0	0	2	1	21.22	77.9	9.5
0	0	3	1	29.84	99.8	5.1-5.8
0	0	4	1	32.11	65.0	2.0
1	1	1	0	16.53	29.0	2.9-7.3
1	2	1	0	19.80	13.0	10.4
1	3	1	0	22.57	5.9	10.7
1	2	-2	0	-13.19	28.9	11.9



**Fig. 7.** Species distribution diagram for (hypydc)<sup>3-</sup> (L) and Ca<sup>2+</sup> (M) at 25 °C and ionic strength 0.1 M KCl.

were obtained *via* the program SPE [46].

## CONCLUSIONS

In this study, a new metal-organic compound of Ca(II) as a pentagonal bipyramidal complex was prepared and structurally characterized by some spectroscopic methods. Based upon the X-ray crystallography results, we can conclude that  $\pi$ - $\pi$  stacking, ion pairing, and intra- and inter-molecular hydrogen bond interactions in the crystal structure play important role in the stabilization of the title crystalline compound. In continuation of the previously reported works by our group containing theoretical data [15-17], here, optimization was done using two standard basis set of 6-31G (d,p) for the single anionic complex (**S**) and LanL2MB basis set for the double anionic complexes (**D**) which describe the electrons of all atoms. As an interesting finding from our theoretical calculations, when we repeated the optimization on the double complexes in the presence of strong hydrogen-bond interaction between two hydroxyl groups, O3-H3A...O8<sup>ii</sup> (ii = x-1, y, z-1), it was revealed that the parallel position of the ligands to each other was exactly like that of the solid state. As it is seen from the figures and tables, the most likely species for the Ca<sup>2+</sup> are HML, the most abundant species in all ranges of pH values, and HML<sub>2</sub>, HML<sub>3</sub>, ML<sub>2</sub>(OH)<sub>2</sub> at higher pH values. There was not any interaction between these species and Q in the condition of solution pH metry.

## SUPPLEMENTARY MATERIAL

CCDC 729858 for C<sub>34</sub>H<sub>48</sub>N<sub>8</sub>O<sub>26</sub>Ca<sub>2</sub> contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail for inquiry: [fileserv@ccdc.cam.ac.uk](mailto:fileserv@ccdc.cam.ac.uk); e-mail for deposition: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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