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Potentiometric and structural studies of M^{II} (Ca, Sr, Ba) -pyridine-2,6-dicarboxylic acid-2-aminopyridine adduct

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Potentiometric measurements and crystal structures of three supramolecular metal-organic compounds, M^{II} (Ca^{II}, Sr^{II}, Ba^{II})-pyridine-2,6-dicarboxylic acid-2-aminopyridine, have been investigated. On the basis of crystallographic data, three supramolecular coordination compounds, $[Ca(pydc)(\mu-H_2O)(H_2O)_2]_n$ (1), $(2-apyH)_2[Sr(pydc)_2(H_2O)_3] \cdot 5H_2O$ (2), and $(2-apyH)_2[Ba(pydc)_2(H_2O)_3] \cdot 5H_2O$ (3) (pydc = pyridine-2,6-dicarboxylate, 2-apy = 2-aminopyridine), were prepared. These compounds form a 3-D structure by a variety of noncovalent interactions such as extensive O–H \cdots O, N–H \cdots O, C–H \cdots O hydrogen bonds, C–O \cdots π , N–H \cdots π , C–H \cdots π , and $\pi\cdots\pi$ interactions. The equilibrium constants for the pydc-2-apy adduct and the stoichiometry and stability of complexation of this adduct with Ca(II), Sr(II) and Ba(II) in aqueous solution were investigated by potentiometric pH titration method. The stoichiometry of the complexes in solution was compared to the crystalline metal ion complexes.

Keywords: Pyridine-2, 6-dicarboxylic acid; 2-Aminopyridine; Supramolecular coordination compound; Crystal structure; Potentiometric study

1. Introduction

Design and construction of metal-organic frameworks (MOFs) have attracted extensive interest because of their applications [1–13]. The ability of aminopyridine (2-amino-, 3-amino- or 4-aminopyridine) and carboxylic acids to form MOF supramolecular architectures is well studied [14–17], and their metal complexes are also investigated because of their applications as chemical reagents in analytical practice and as luminophores in supramolecular photochemistry [16]. Pyridine-2,6-dicarboxylic acid has been used in many areas of science, such as coordination chemistry, biochemistry, and medical chemistry [18–23]. Some experimental results show aminopyridine is a monodentate ligand, binding through pyridine nitrogen, attributed to stronger basicity of another nitrogen [14, 24–28].

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The potentiometric method has been used extensively in many branches of solution chemistry, since it is fast and easy. Binary and ternary complexes of transition metals with molecules of biological and pharmaceutical interest have been studied [29–34]. Research on MOFs has generally centered on the assembly of organic linkers with metal ions. The chemistry of alkaline earth metals has been an undeveloped area of coordination chemistry [34]. Owing to their higher coordination number and more flexible coordination geometry, alkaline earth metals should produce structures with topologies different from transition metals [35].

As continuation of our research on MOFs [36–45], we were inspired to explore further by adding another organic ligand to the reaction mixture of pyridine-2,6-dicarboxylic acid and metals in order to construct coordination compounds. We report the synthesis and systematic structural behavior of Ca(II), Sr(II), and Ba(II) supramolecular coordination compounds with pyridine-2,6-dicarboxylic acid and 2-aminopyridine adduct. Furthermore, the equilibrium potentiometric pH titration profiles of pyridine-2,6-dicarboxylic acid and 2-aminopyridine and their mixture were obtained in the absence and presence of the Ca(II), Sr(II), and Ba(II) ions. Solution studies reveal expected species present in solution and compare well to the solid state.

2. Experimental setup

2.1. Reagents and apparatus

All chemicals were from commercial suppliers and used without purification. Doubly distilled deionized water was used in the procedures when needed. Melting points were determined with an Electrothermal IA-9100 and were not corrected. IR spectra were recorded on an 843 Perkin-Elmer spectrophotometer using KBr discs. Elemental analyzes (C, H, and N) were carried out with a Perkin-Elmer 2400 CHN elemental analyzer. X-ray data were obtained with a Bruker SMART diffractometer. Single crystals of all the compounds suitable for crystallography were selected. Unit cell determination and data collection of the compounds were collected on a Bruker SMART CCD area detector system using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) [46]. The structures were solved and refined by full-matrix least-squares techniques on F^2 using SHELX-97 (SHELXL program package) [47].

2.2. Potentiometric equilibrium measurements

A Model 794 Metrohm Basic Titrino was attached to an extension combined glass-calomel electrode mounted in an air-protected, sealed, thermostated jacketed cell maintained at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ 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 $-\log [\text{H}^+]$.

2.3. Synthesis of $[\text{Ca}(\text{pydc})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]_n$ (1)

An aqueous solution of pyridine-2,6-dicarboxylic acid (54 mg, 0.33 mM) and 2-aminopyridine (31 mg, 0.33 mM) in water (20 mL) was added to a solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (38 mg, 0.16 mM) in water (10 mL) and refluxed for 12 h. Prism colorless crystals of the

complex, suitable for X-ray analysis, were obtained by slow evaporation of the solution at room temperature after six weeks. And then decomposed at >400 °C. Anal. Calcd for $C_7H_9CaNO_7$ (%): C, 32.4; H, 3.4; N, 5.4. Found: C, 32.2; H, 3.3; N, 5.6.

2.4. Synthesis of $(2\text{-apyH})_2[\text{Sr}(\text{pydc})_2(\text{H}_2\text{O})_3]\cdot 5\text{H}_2\text{O}$ (2)

The experimental procedure for preparation of $(2\text{-apyH})_2[\text{Sr}(\text{pydc})_2(\text{H}_2\text{O})_3]\cdot 5\text{H}_2\text{O}$ was similar to that of **1** with replacement of $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ by $\text{Sr}(\text{NO}_3)_2$ (34 mg, 0.16 mM). Plate colorless crystals of this compound were obtained by slow evaporation at room temperature after eight weeks. m.p.: 258 °C. Anal. Calcd for $C_{24}H_{36}N_6O_{16}\text{Sr}$ (%): C, 38.3; H, 4.8; N, 11.2. Found: C, 38.1; H, 4.3; N, 11.0.

2.5. Synthesis of $(2\text{-apyH})_2[\text{Ba}(\text{pydc})_2(\text{H}_2\text{O})_3]\cdot 5\text{H}_2\text{O}$ (3)

Preparation of $(2\text{-apyH})_2[\text{Ba}(\text{pydc})_2(\text{H}_2\text{O})_3]\cdot 5\text{H}_2\text{O}$ was carried out similar to that of **1** by using $\text{Ba}(\text{NO}_3)_2$ (42 mg, 0.16 mM). Prism colorless crystals of this compound were obtained after five weeks. m.p.: 220 °C. Anal. Calcd for $C_{24}H_{36}\text{BaN}_6\text{O}_{16}$ (%): C, 36.0; H, 4.5; N, 10.5. Found: C, 36.1; H, 4.1; N, 10.8.

2.6. Potentiometric studies procedure

The details are described in [37, 38, 48–50]. The concentration of 2-apy and pydc was 2.50×10^{-3} M, for the potentiometric pH titrations of pydc, 2-apy and pydc-2-apy, in the absence and presence of 1.25×10^{-3} metal ions. A standard carbonate-free NaOH solution (0.0983 M) was used in all titrations. The ionic strength was adjusted to 0.1 M with KNO_3 . Before an experimental point (pH) was measured, sufficient time was allowed for the establishment of equilibrium. Ligand protonation constants and stability constants of adduct and their metal complexes were evaluated using the BEST program [51] and the corresponding distribution diagrams were depicted using Hyss2009 as a new version of older [52]. The value of $K_w = [\text{H}^+][\text{OH}^-]$ used in the calculations according to our previous works [37, 48, 49].

3. Results and discussion

3.1. X-ray crystallographic structure of **1**

The procedure adopted in the synthesis of $[\text{Ca}(\text{pydc})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]_n$ is outlined in scheme 1. The reaction of $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ with pyridine-2,6-dicarboxylic acid and 2-aminopyridine adduct in aqueous solution leads to the formation of **1**. The crystal structure and layered packing diagram of $[\text{Ca}(\text{pydc})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]_n$ are shown in figures 1 and 2, respectively. A summary of crystallographic data is given in table 1. Selected bond lengths and angles are presented in tables 2 and 3, respectively. Also a list of inter and intramolecular hydrogen bonds is given in table 4.

This complex crystallizes in monoclinic $P2_1/n$ space group. In preparation of the complex, we used pydcH_2 and 2-apy as proton donor and proton acceptor, but the result

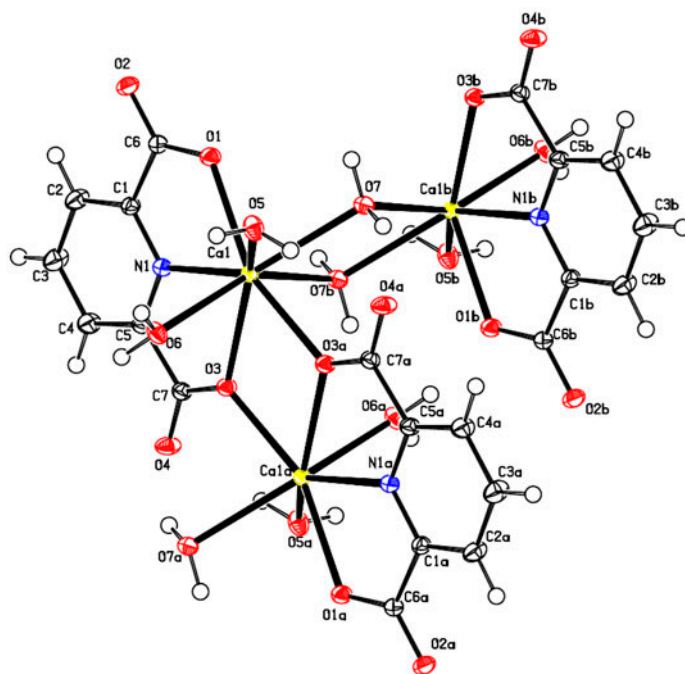


Figure 1. The molecular structure of **1** showing the atom numbering scheme.

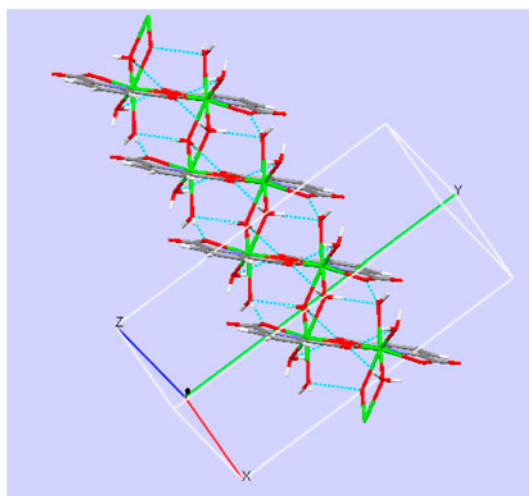


Figure 2. A layered packing diagram of **1**.

was different, which proved that just pydc^{2-} contributed to the molecular structure of **1**, forming a 3-D coordination polymer as shown in figure 1. The aminopyridine molecules did not incorporate in the structure, although they were used in the synthesis procedure.

Table 1. Crystallographic data for 1–3.

	1	2	3
Empirical formula	C ₇ H ₉ CaNO ₇	C ₂₄ H ₃₆ BaN ₆ O ₁₆	C ₂₄ H ₃₆ N ₆ O ₁₆ Sr
Formula weight	259.23	801.93	752.21
Temperature (K)	120(2)	120(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> <i>Z</i> = 4	<i>P</i> 2 ₁ / <i>c</i> <i>Z</i> = 4	<i>C</i> 2/ <i>c</i> <i>Z</i> = 4
Unit cell dimensions	<i>a</i> = 5.8549(7) Å <i>b</i> = 17.911(2) Å <i>c</i> = 9.834(1) Å β = 98.219(2)°	<i>a</i> = 13.457(3) Å <i>b</i> = 13.193(3) Å <i>c</i> = 17.948(4) Å β = 96.07 (2)°	<i>a</i> = 20.987(2) Å <i>b</i> = 20.117(9) Å <i>c</i> = 13.428(9) Å β = 123.084(2)°
Absorption coefficient (mm ⁻¹)	0.636	1.336	1.826
Crystal dimensions (mm ³)	0.20 × 0.15 × 0.12	0.35 × 0.18 × 0.12	0.30 × 0.20 × 0.15
<i>F</i> (000)	536	1624	1552
θ Range for data collection (°)	2.27–30.05	1.52–27.50	3.00–27.00
Index ranges	−8 ≤ <i>h</i> ≤ 8 −25 ≤ <i>k</i> ≤ 25 −13 ≤ <i>l</i> ≤ 13	−17 ≤ <i>h</i> ≤ 17 −17 ≤ <i>k</i> ≤ 17 −23 ≤ <i>l</i> ≤ 23	−26 ≤ <i>h</i> ≤ 26 −16 ≤ <i>k</i> ≤ 16 −17 ≤ <i>l</i> ≤ 17
Reflections collected	2974	7275	3349
Goodness of fit on <i>F</i> ²	1.001	0.948	1.020
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0363 <i>wR</i> 2 = 0.0856	<i>R</i> 1 = 0.0377 <i>wR</i> 2 = 0.0566	<i>R</i> 1 = 0.0339 <i>wR</i> 2 = 0.0763
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0394 <i>wR</i> 2 = 0.0883	<i>R</i> 1 = 0.0696 <i>wR</i> 2 = 0.0599	<i>R</i> 1 = 0.0429 <i>wR</i> 2 = 0.0795
Largest diff. peak and hole (e.Å ⁻³)	0.000–0.001	0.000–0.003	0.000–0.001

Table 2. Selected bond lengths (Å) of 1–3.

[Ca(pydc)(μ -H ₂ O)(H ₂ O) ₂] _n (1)			
Ca(1)–O(1)	2.4148(11)	Ca(1)–O(6)	2.4114(11)
Ca(1)–O(3)	2.5321(10)	Ca(1)–O(7)	2.5862(11)
Ca(1)–O(3a)	2.3753(10)	Ca(1)–O(7b)	2.4334(11)
Ca(1)–O(5)	2.5222(11)	Ca(1)–N(1)	2.5019(12)
(2-apyH) ₂ [Sr(pydc) ₂ (H ₂ O) ₃]·5H ₂ O (2)			
Sr(1)–O(1)	2.69374(15)	Sr(1)–O(2W)	2.6647(18)
Sr(1)–O(3)	2.6353(14)	Sr(1)–N(1)	2.8006(17)
Sr(1)–O(1W)	2.546(3)		
(2-apyH) ₂ [Ba(pydc) ₂ (H ₂ O) ₃]·5H ₂ O (3)			
Ba(1)–O(2)	2.881(3)	Ba(1)–O(16)	2.770(3)
Ba(1)–O(3)	2.840(3)	Ba(1)–O(16')	2.797(3)
Ba(1)–O(4)	2.743(3)	Ba(1)–N(5)	2.911(3)
Ba(1)–O(13)	2.797(3)	Ba(1)–N(5')	2.935(3)
Ba(1)–O(13')	2.771(3)		

In the crystal structure, Ca(1) is coordinated by one nitrogen and two oxygens from pyridine-2,6-dicarboxylate and also by two oxygens from water. In this polymeric complex, pyridine-2,6-dicarboxylate and water bridge two Ca(II) ions. The units are then linked into an infinite system via additional Ca–O bonds. The calciums are connected via a four-membered ring Ca₂O₂. There exists two types of four-membered Ca₂O₂ rings with Ca···Ca distances of 4.009 Å, Ca(1) and Ca(1a) bridged by O(3) and O(3a), and 4.193 Å, Ca(1) and Ca(1b) bridged by O(7) and O(7b) atoms.

Table 3. Selected bond angles (°) of **1–3**.

[Ca(pydc)(μ -H ₂ O)(H ₂ O) ₂] _n (1)						
O(1)–Ca(1)–O(3)	127.51(4)	O(3)–Ca(1)–O(7b)	77.75(3)	O(1)–Ca(1)–N(1)	64.74(4)	
O(1)–Ca(1)–O(3a)	158.71(4)	O(3a)–Ca(1)–O(5)	84.75(4)	O(3)–Ca(1)–N(1)	63.39(4)	
O(1)–Ca(1)–O(5)	84.98(4)	O(3a)–Ca(1)–O(6)	86.15(4)	O(3a)–Ca(1)–N(1)	133.74(4)	
O(1)–Ca(1)–O(6)	108.53(4)	O(3a)–Ca(1)–O(7)	77.75(3)	O(5)–Ca(1)–N(1)	134.55(4)	
O(1)–Ca(1)–O(7)	81.06(4)	O(3a)–Ca(1)–O(7b)	79.14(4)	O(6)–Ca(1)–N(1)	84.93(4)	
O(1)–Ca(1)–O(7b)	94.48(4)	O(5)–Ca(1)–O(6)	73.06(4)	O(7)–Ca(1)–N(1)	133.50(4)	
O(3)–Ca(1)–O(3a)	70.48(4)	O(5)–Ca(1)–O(7)	66.80(3)	O(7b)–Ca(1)–N(1)	84.78(4)	
O(3)–Ca(1)–O(5)	84.75(4)	O(5)–Ca(1)–O(7b)	133.00(4)	Ca(1)–O(3)–Ca(1a)	109.52(4)	
O(3)–Ca(1)–O(6)	74.40(4)	O(6)–Ca(1)–O(7)	137.74(4)	Ca(1)–O(7)–Ca(1b)	113.29(4)	
O(3)–Ca(1)–O(7)	132.78(3)	O(6)–Ca(1)–O(7b)	147.65(4)			
(2-apyH) ₂ [Sr(pydc) ₂ (H ₂ O) ₃]·5H ₂ O (2)						
O(1)–Sr(1)–O(1a)	161.46(7)	O(1a)–Sr(1)–O(3a)	115.80(4)	O(2W)–Sr(1)–N(1)	77.65(5)	
O(1)–Sr(1)–O(1W)	80.73(4)	O(1a)–Sr(1)–N(1)	117.19(5)	O(2W)–Sr(1)–N(1a)	126.12(5)	
O(1)–Sr(1)–O(2W)	69.10(5)	O(1a)–Sr(1)–N(1a)	58.11(5)	O(2Wa)–Sr(1)–O(3)	86.96(5)	
O(1)–Sr(1)–O(2Wa)	129.02(6)	O(1W)–Sr(1)–O(2W)	147.87(4)	O(2Wa)–Sr(1)–O(3a)	93.58(5)	
O(1)–Sr(1)–O(3)	115.80(4)	O(1W)–Sr(1)–O(2Wa)	147.87(4)	O(2Wa)–Sr(1)–N(1)	126.12(5)	
O(1)–Sr(1)–O(3a)	64.08(4)	O(1W)–Sr(1)–O(3)	89.68(4)	O(2Wa)–Sr(1)–N(1a)	77.65(5)	
O(1)–Sr(1)–N(1)	58.11(5)	O(1W)–Sr(1)–O(3a)	89.68(4)	O(3)–Sr(1)–O(3a)	179.37(7)	
O(1)–Sr(1)–N(1a)	117.19(5)	O(1W)–Sr(1)–N(1)	77.19(4)	O(3)–Sr(1)–N(1)	57.86(5)	
O(1a)–Sr(1)–O(1W)	80.73(4)	O(1W)–Sr(1)–N(1a)	77.19(4)	O(3)–Sr(1)–N(1a)	121.98(5)	
O(1a)–Sr(1)–O(2W)	129.02(6)	O(2W)–Sr(1)–O(2Wa)	64.25(8)	O(3a)–Sr(1)–N(1)	121.98(5)	
O(1a)–Sr(1)–O(2Wa)	69.10(5)	O(2W)–Sr(1)–O(3)	93.58(5)	O(3a)–Sr(1)–N(1a)	57.86(5)	
O(1a)–Sr(1)–O(3)	64.08(4)	O(2W)–Sr(1)–O(3a)	86.96(5)			
(2-apyH) ₂ [Ba(pydc) ₂ (H ₂ O) ₃]·5H ₂ O (3)						
O(2)–Ba(1)–O(3)	62.54(6)	O(3)–Ba(1)–O(16')	70.86(8)	O(13)–Ba(1)–N(5)	56.29(8)	
O(2)–Ba(1)–O(4)	145.16(8)	O(3)–Ba(1)–N(5)	123.68(8)	O(13)–Ba(1)–N(5')	122.60(8)	
O(2)–Ba(1)–O(13)	97.12(9)	O(3)–Ba(1)–N(5')	79.93(8)	O(13')–Ba(1)–O(16)	66.06(7)	
O(2)–Ba(1)–O(13')	87.24(9)	O(4)–Ba(1)–O(13)	83.86(10)	O(13')–Ba(1)–O(16')	111.62(8)	
O(2)–Ba(1)–O(16)	68.47(8)	O(4)–Ba(1)–O(13')	91.08(10)	O(13')–Ba(1)–N(5)	122.62(8)	
O(2)–Ba(1)–O(16')	130.97(8)	O(4)–Ba(1)–O(16)	79.09(9)	O(13')–Ba(1)–N(5')	55.87(8)	
O(2)–Ba(1)–N(5)	77.50(8)	O(4)–Ba(1)–O(16')	81.64(9)	O(16)–Ba(1)–O(16')	160.51(7)	
O(2)–Ba(1)–N(5')	125.08(8)	O(4)–Ba(1)–N(5)	74.26(9)	O(16)–Ba(1)–N(5)	56.81(9)	
O(3)–Ba(1)–O(4)	152.09(8)	O(4)–Ba(1)–N(5')	80.80(9)	O(16)–Ba(1)–N(5')	117.50(8)	
O(3)–Ba(1)–O(13)	89.73(9)	O(13)–Ba(1)–O(13')	174.93(8)	O(16')–Ba(1)–N(5)	120.09(9)	
O(3)–Ba(1)–O(13')	94.61(9)	O(13)–Ba(1)–O(16)	113.10(8)	O(16')–Ba(1)–N(5')	55.84(9)	
O(3)–Ba(1)–O(16)	128.00(8)	O(13)–Ba(1)–O(16')	67.36(8)	N(5)–Ba(1)–N(5')	155.03(8)	

Table 4. Inter and intramolecular hydrogen bonds for **1**.

D–H	A	d(D–H)	d(H···A)	d(D···A)	∠DHA	Symmetry codes
O(5)–H(5A)	O(2)	0.91	1.85	2.723(2)	160	$x - 1/2, -y + 3/2, z + 1/2$
O(5)–H(5B)	O(4)	0.91	2.09	2.873(2)	144	$-x, -y + 1, -z + 1$
O(6)–H(6A)	O(2)	0.90	1.83	2.717(2)	167	$x - 1/2, -y + 3/2, z + 1/2$
O(6)–H(6B)	O(1)	0.92	1.80	2.697(2)	164	$x - 1, y, z$
O(7)–H(7A)	O(4)	0.91	1.89	2.693(2)	147	$-x, -y + 1, -z + 1$
O(7)–H(7B)	O(6)	0.92	1.99	2.859(2)	157	$x + 1, y, z$
C(4)–H(4A)	O(4)	0.95	2.26	3.183(2)	163	$-1 - x, 1 - y, -z$

In **1**, Ca1(II) is coordinated by one nitrogen and seven oxygens in a distorted bicapped trigonal antiprismatic coordination geometry (eight-coordinate), with O(3), O(5), O(6), O(7), O(7b), and N(1) forming one trigonal antiprism, and O(1) and O(3a) forming two caps (figure 3). The only Ca(1)–N(1) bond length is 2.5019(12) Å and the seven Ca(1)–O bond lengths are between 2.3753(10) and 2.5862(11) Å.

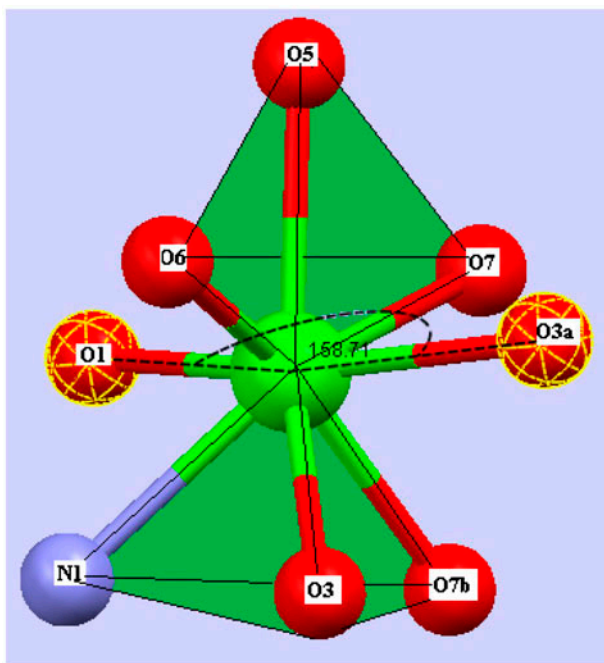


Figure 3. Distorted bicapped trigonal antiprismatic coordination geometry for **1**.

3.1.1. Description of noncovalent interactions in $[\text{Ca}(\text{pydc})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]_n$ (1**).** The noncovalent interactions in the crystal packing of this complex are hydrogen bonding and π stacking, which link the fragments of the crystal lattice. A number of O–H \cdots O hydrogen bonds with D \cdots A distances ranging from 2.6932(15) to 2.8731(17) Å are observed in the crystal packing. The strongest hydrogen bonds are O(5)–H(5A) \cdots O(2) [symmetry code: $x - 1/2, -y + 3/2, z + 1/2$], O(6)–H(6A) \cdots O(2) [symmetry code: $x - 1/2, -y + 3/2, z + 1/2$] and O(6)–H(6B) \cdots O(1) [symmetry code: $x - 1, y, z$] (table 4). Here, organized weak interactions between C(4)–H(4A) and O(4) [symmetry code: $-1 - x, 1 - y, -z$] contribute to the supramolecular arrangement (figure 4).

In the crystal structure, C–O $\cdots\pi$ stacking was observed between C(6)–O(2) and pyridine rings (N1, C1–C5), with distance of 3.704 Å and angle 98.80° (figure 5).

3.2. X-ray crystallographic structure of **2** and **3**

The reaction between pyridine-2,6-dicarboxylic acid and 2-aminopyridine with strontium(II) nitrate and/or barium(II) nitrate were carried out and crystalline compound $(2\text{-apyH})_2[\text{M}(\text{pydc})_2(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$ (M = Sr, Ba) was obtained by slow evaporation of solvent at room temperature (scheme 1).

The crystallographic data of these compounds are given in table 1. Selected bond lengths and angles are listed in tables 2 and 3, respectively. Inter and intramolecular hydrogen bond geometries are shown in tables 5 and 6. Views of the molecular structures of **2** and **3** are shown in figures 6 and 7, respectively.

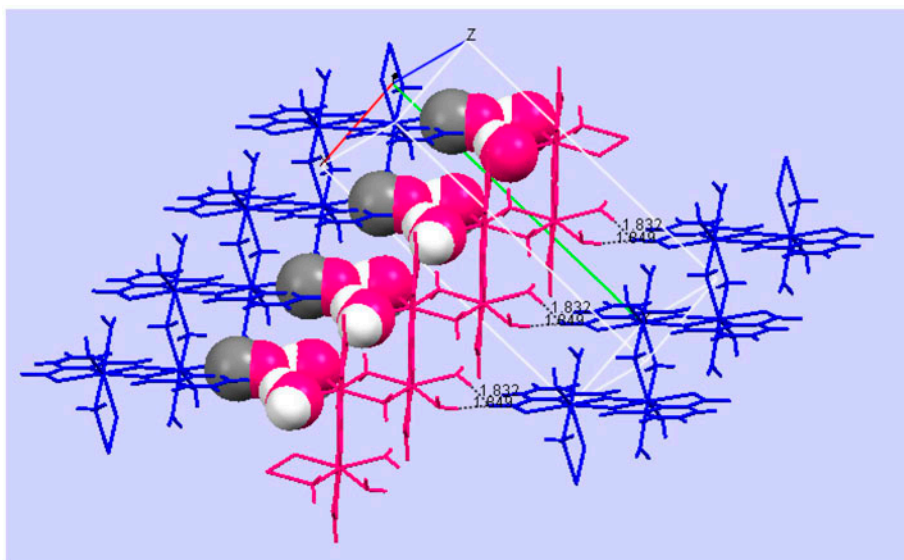


Figure 4. Weak hydrogen bond interactions between C(4)–H(4A) and O(4) [symmetry code: $-1-x, 1-y, -z$] to form supramolecular arrangements.

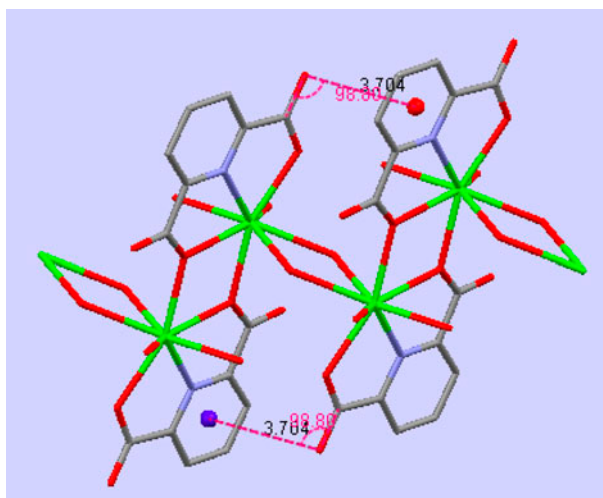
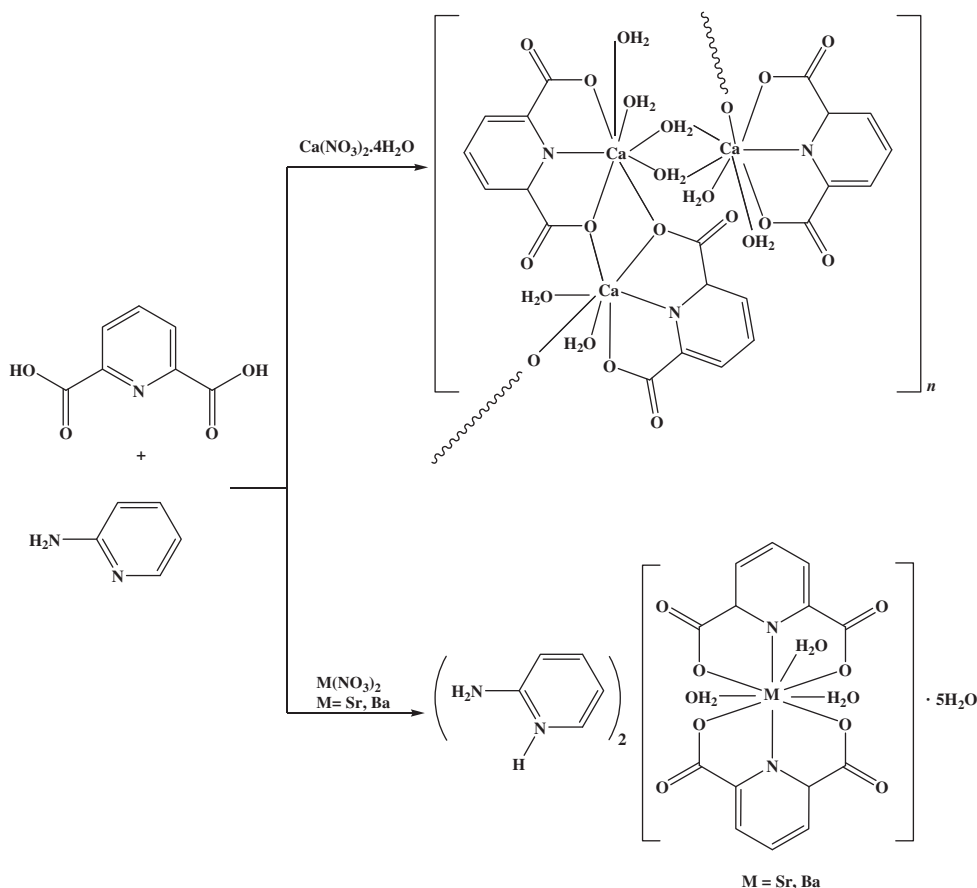


Figure 5. C–O \cdots π interaction in **1**. The hydrogens are omitted for clarity.

The crystal structures of **2** and **3** are very similar; in the anionic complexes of **2** and **3**, $[M(\text{pydc})_2(\text{H}_2\text{O})_3]^{2-}$, the M(II) ($M = \text{Sr}, \text{Ba}$) is nine-coordinate by two nitrogens and four oxygens of carboxylates of two $(\text{pydc})^{2-}$ fragments and three waters. All M–O and M–N bonds are not equal to each other (table 2). The average values of Sr–O and Sr–N bond lengths are also in agreement with previous reports of strontium(II) complexes with pyridine-2,6-dicarboxylate. Average values of Ba–O and Ba–N bond lengths are comparable



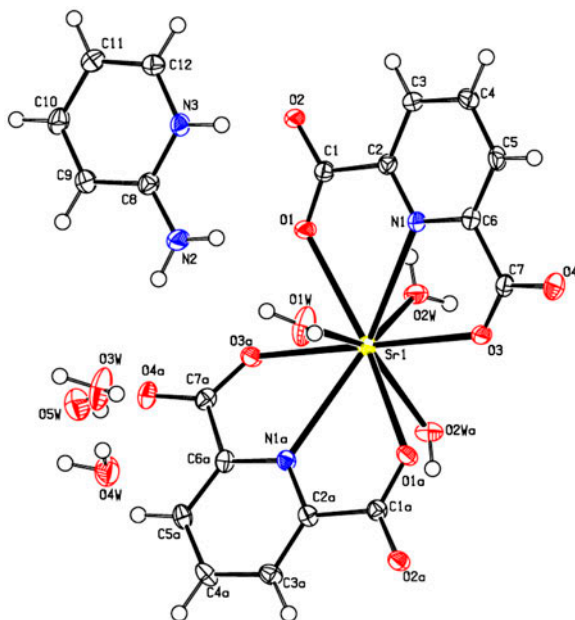
Scheme 1. The synthesis of $[\text{Ca}(\text{pydc})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]_n$, $(2\text{-apyH})_2[\text{Sr}(\text{pydc})_2(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$, and $(2\text{-apyH})_2[\text{Ba}(\text{pydc})_2(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$.

Table 5. Inter and intramolecular hydrogen bonds for **2**.

D-H	A	d(D-H)	d(H...A)	d(D...A)	$\angle\text{DHA}$	Symmetry codes
N(2)-H(1N2)	O(1)	0.88(4)	1.98(4)	2.858(3)	175.9(18)	
N(2)-H(1N2)	O(3)	0.88(4)	2.48(4)	2.827(3)	104(3)	$-x+1, y, -z+1/2$
N(2)-H(2N2)	O(3)	0.88(4)	2.52(3)	2.827(3)	101(3)	$-x+1, y, -z+1/2$
N(2)-H(2N2)	O(4)	0.88(4)	2.37(4)	3.175(3)	154(3)	$-x+1, y, -z+1/2$
N(3)-H(1N3)	O(2)	0.94(4)	1.74(4)	2.673(3)	174(3)	
O(1W)-H(1W1)	O(4)	0.82(3)	2.02(3)	2.833(2)	169(5)	$x, -y, z+1/2$
O(2W)-H(2W2)	O(4W)	0.80(3)	1.95(3)	2.749(3)	174(3)	$-x+1, -y+1, -z+1$
O(2W)-H(1W2)	O(2)	0.77(4)	2.04(4)	2.786(3)	161(4)	$-x+3/2, -y+1/2, -z+1$
O(3W)-H(1W3)	O(4)	0.86(3)	1.90(3)	2.756(2)	174(3)	$-x+1, y, -z+1/2$
O(4W)-H(2W4)	O(5W)	0.88(3)	1.83(3)	2.714(3)	175(4)	$-x+1, -y+1, -z+2$
O(4W)-H(1W4)	O(3W)	0.80(3)	2.05(3)	2.839(3)	173(4)	
O(5W)-H(2W5)	O(3)	0.82(4)	1.93(4)	2.716(3)	160(4)	$-x+1, -y+1, -z+1$
O(5W)-H(1W5)	O(2W)	0.77(4)	2.26(4)	2.978(3)	156(4)	$x, -y+1, z+1/2$
C(4)-H(10A)	O(4W)	0.95	2.57	3.504(4)	167	$1/2+x, 1/2-y, -1/2+z$

Table 6. Inter and intramolecular hydrogen bonds for 3.

D-H	A	d(D-H)	d(H...A)	d(D...A)	∠DHA	Symmetry codes
O(1W)-H(2W)	O(3W)	0.85	1.99	2.841(4)	176	$-x+1, -y+1, -z$
O(1W)-H(1W)	O(2W)	0.85	1.91	2.740(5)	167	
O(2)-H(2B)	O(15')	0.85	1.96	2.798(3)	168	$x, -y+3/2, z+1/2$
O(2)-H(2A)	O(1W)	0.87	1.86	2.731(4)	177	$x, y+1, z$
O(2W)-H(3W)	O(13)	0.85	1.94	2.760(5)	164	$-x+1, -y+1, -z$
O(2W)-H(4W)	O(3)	0.85	2.17	2.919(4)	148	$-x+1, -y+1, -z$
O(3)-H(3B)	O(15)	0.80	1.95	2.746(3)	173	$x, -y+3/2, z-1/2$
O(3)-H(3A)	O(4W)	0.92	1.85	2.762(4)	174	$x, y+1, z-1$
O(3W)-H(5W)	O(12')	0.85	1.91	2.750(4)	171	$x+1, y, z$
O(3W)-H(6W)	O(12)	0.85	1.88	2.727(4)	174	
O(4W)-H(7W)	O(3W)	0.85	1.95	2.794(4)	172	$-x+1, -y+1, -z+1$
O(4W)-H(8W)	O(5W)	0.85	1.95	2.750(5)	157	$-x, -y+1, -z+1$
O(4)-H(4B)	O(12)	0.84	1.97	2.801(4)	169	$-x+1, -y+1, -z$
O(4)-H(4A)	O(12')	0.89	1.90	2.787(4)	171	$-x, -y+1, -z$
O(5W)-H(9W)	O(2)	0.85	2.14	2.913(4)	151	
O(5W)-H(10W)	O(13')	0.85	1.93	2.746(5)	160	
N(1K)-H(1K)	O(15')	0.90	1.79	2.674(5)	168	$x+1, y, z$
N(1L)-H(1L)	O(15')	0.90	1.79	2.682(4)	169	$x, y, z+1$
N(7K)-H(7KB)	O(12')	0.90	2.55	3.386(4)	154	$x+1, y, z$
N(7K)-H(7KA)	O(16)	0.90	1.99	2.884(4)	177	$x+1, y, z$
N(7L)-H(7LB)	O(16')	0.90	1.97	2.861(5)	169	$x, y, z+1$
N(7K)-H(7KB)	O(13')	0.90	2.54	2.866(4)	102	$x+1, y, z$
C(8)-H(8)	O(1W)	0.95	2.51	3.441(5)	168	$1-x, 1/2+y, 1/2-z$
C(8')-H(8')	O(4W)	0.95	2.57	3.497(5)	166	$-x, 1/2+y, 1/2-z$

Figure 6. The molecular structure of $(2\text{-apyH})_2[\text{Sr}(\text{pydc})_2(\text{H}_2\text{O})_3]\cdot 5\text{H}_2\text{O}$ showing the atom numbering scheme.

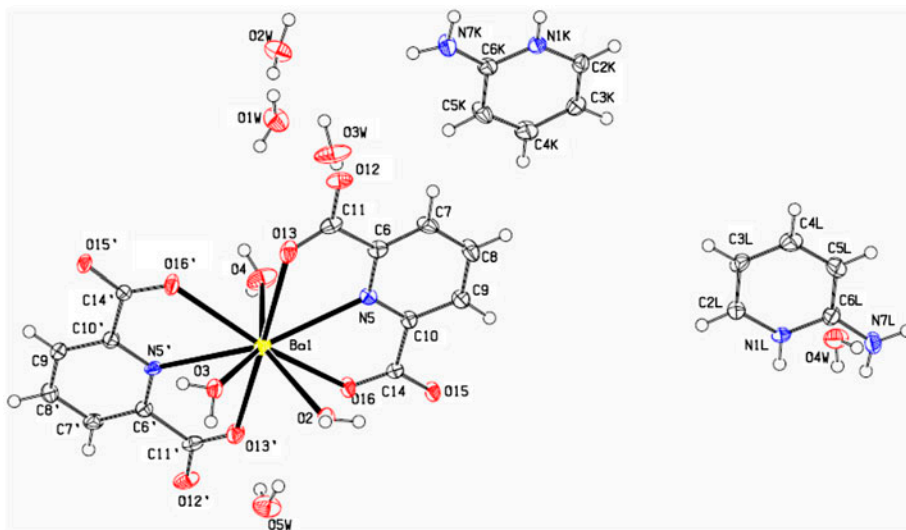


Figure 7. A view of the molecular structure of **3** showing the atom numbering scheme.

with the corresponding ones reported in the literature for related barium(II) complexes with pyridine-3,5-dicarboxylate [38]. The sum of bond angles, O(1)–Sr(1)–O(3), O(1)–Sr(1)–N(1a), O(3)–Sr(1)–N(1a) in **2** and O(13)–Ba(1)–O(16), O(13)–Ba(1)–N(5'), O(16)–Ba(1)–N(5') in **3** is equal to 354.97°. The five oxygens and one nitrogen, O(1), O(1W), O(2W), O(2Wa), O(3), N(1), form trigonal antiprismatic and two oxygens and one nitrogen, O(1), O(3), N(1a), form three caps in distorted tricapped trigonal antiprismatic geometry around Sr(II). Also, in Ba(II) compound O(2), O(3), O(4), O(13'), O(16'), N(5) form trigonal antiprismatic and O(13), O(16), N(5') form three caps in distorted trigonal antiprismatic geometry. Considering the angles between oxygens in both **2** and **3**, they are almost staggered. So, an antiprism consisting of five oxygens and one nitrogen with three caps of two oxygens and one nitrogen on its faces is proposed for both (figures 8 and 9).

3.2.1. Description of noncovalent interactions in (2-apyH)₂[Sr(pydc)₂(H₂O)₃]·5H₂O (2). The crystal lattice is aggregated through intermolecular interactions, such as electrostatic attraction between ion pairs, different kinds of hydrogen bonding, and π stacking interactions.

In the structure of **2**, the complicated network of intra and intermolecular N–H···O, O–H···O and C–H···O hydrogen bonds with D···A distances ranging from 2.673(3) to 3.504(4) Å (table 5) results in complicated networks and cause further stabilization for crystalline graph set descriptors formed in different directions as shown in figure 10. Hydrogen bonding motifs are commonly used by set notation of generalized from $G_b^a(n)$ (G is general formation such as R for ring, C for chain; a and b present the numbers of acceptor and donor atoms, respectively; n denotes the numbers of atoms in the pattern) [53]. Hydrogen bonding interactions between solvent water, O(3W), O(4W), O(5W) result in water clusters that can be described as $C_4^4(15)$ in Etter's notation, where they also interact with anionic complex fragment. The water clusters in the crystal structure of **2** have O···O distances of 1.832–2.048 Å (figure 10). Other O–H···O hydrogen bonds between water, O(3W) and

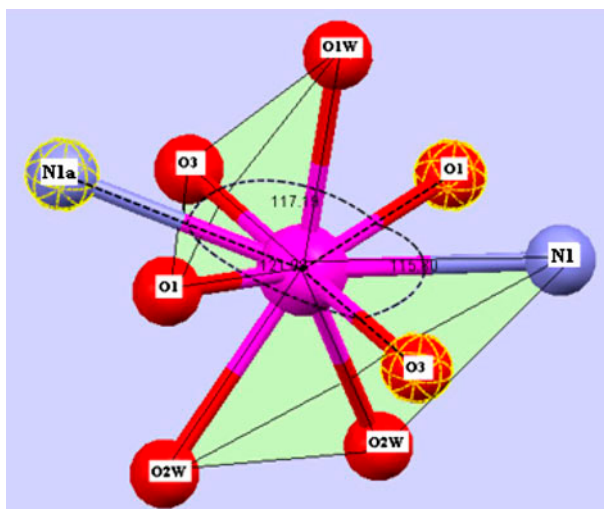


Figure 8. Tricapped trigonal antiprismatic coordination geometry for **2**.

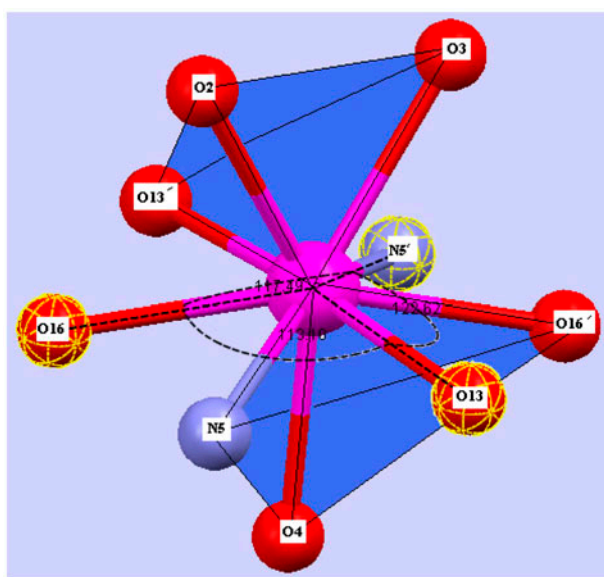


Figure 9. Tricapped trigonal antiprismatic coordination geometry for **3**.

O(4W), and coordinated water, O(2W), in each anionic complex form annular $R_5^5(15)$ **I** and $R_4^4(12)$ **II** patterns in butterfly-like 3-D layer fashion (figures 10 and 11). The other hydrogen bonds, including N–H \cdots O and C–H \cdots O, are held between (2-apyH) $^+$, its counter anion and water. The strongest hydrogen bond with the nearest angle to linear, which can be classified as a strong bond [54], is N(2)–H(1N2) \cdots O(1) and N(3)–H(1N3) \cdots O(2) (table 5). Study of the packing diagram of **2** confirms that the crystalline network is

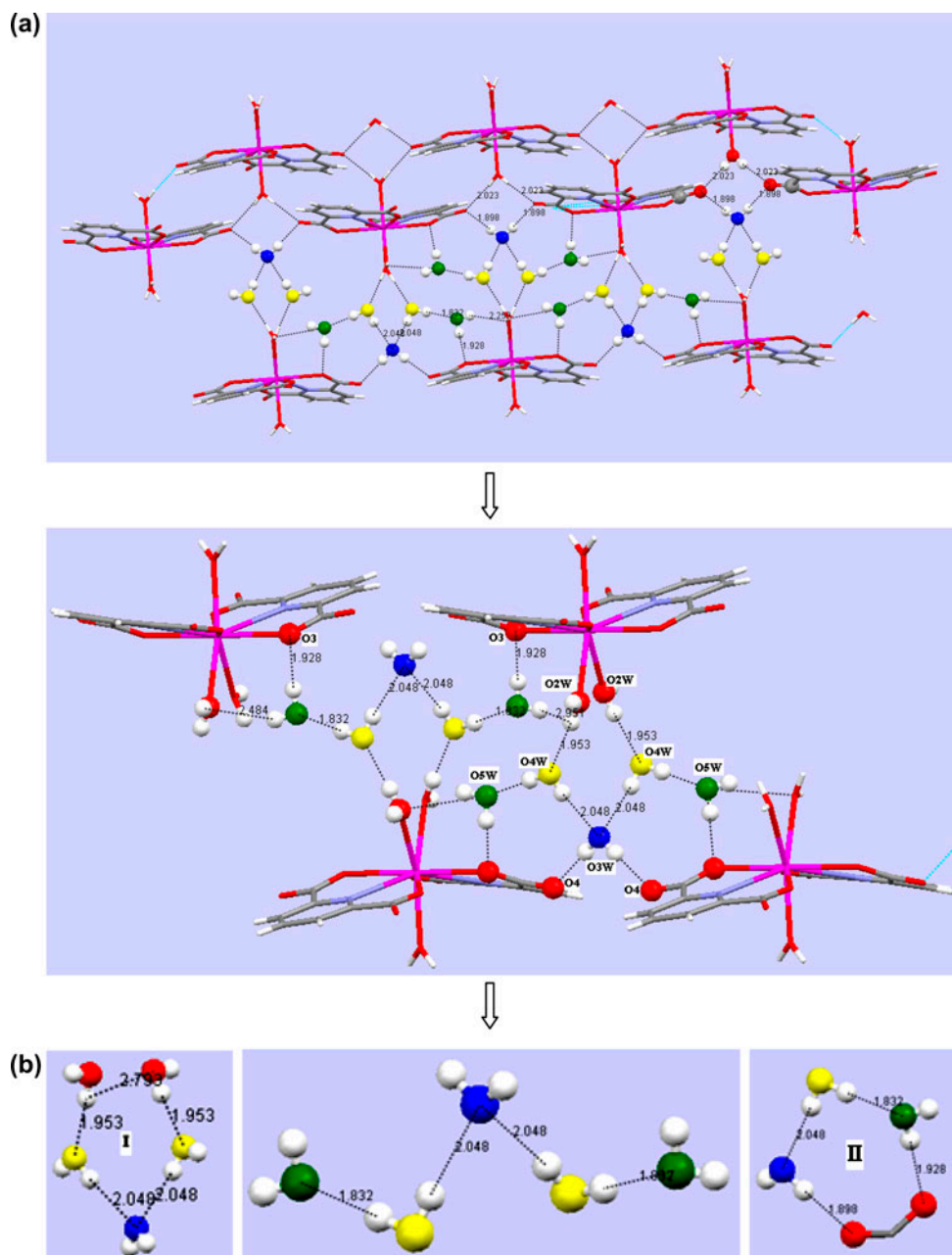


Figure 10. (a) Crystal packing structure of **2** forming a 3-D supramolecular structure from hydrogen bonds. (b) A view of water clusters in chain motifs by O–H···O interactions between water molecules and $[\text{Sr}(\text{pydc})_2(\text{H}_2\text{O})_3]^{2-}$.

strongly stabilized via a complicated network of hydrogen bonding between water and both cationic and anionic units. The spaces between two layers of $[\text{Sr}(\text{pydc})_2(\text{H}_2\text{O})_3]^{2-}$ and $(2\text{-apyH})^+$ fragments are filled with uncoordinated water (figure 12).

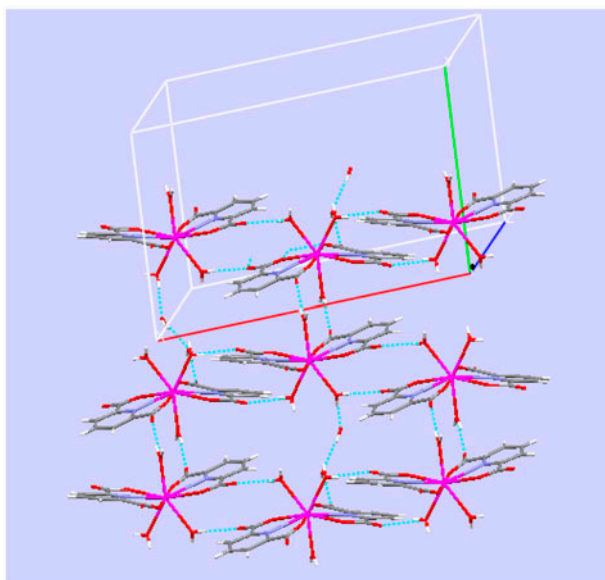


Figure 11. Hydrogen bonding in butterfly-like 3-D layer fashion in **2**.

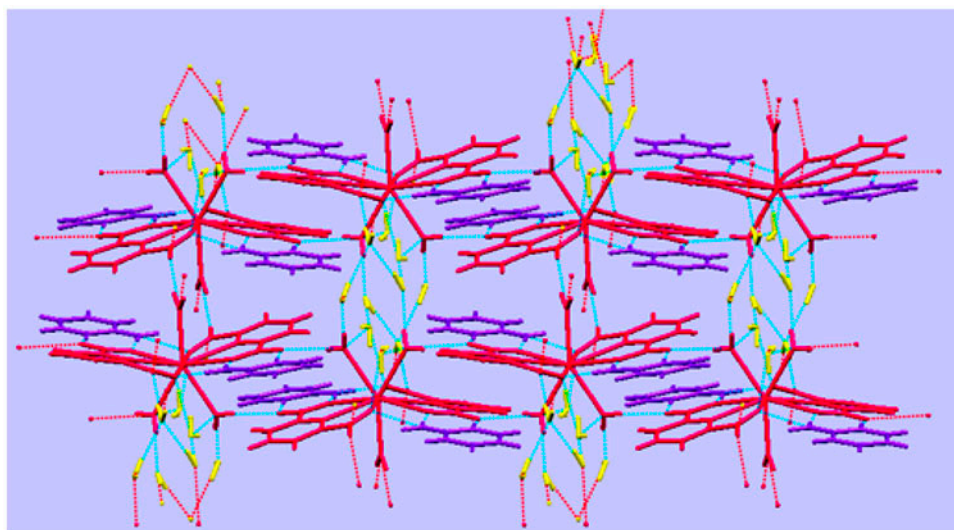


Figure 12. Crystal packing diagram of **2**; hydrogen bonds are shown as dashed lines.

Intermolecular interactions that can be observed in **2** are C–H \cdots π , N–H \cdots π and $\pi\cdots\pi$ stacking interactions. The N–H \cdots π interaction is N(3)–H(1)/N1,C1–C6 with distance (measured to the center of the ring) of 3.232 Å and N–H \cdots π angle of 82.26° (figure 13). The strongest C–H \cdots π is between C(5)–H(15a)/N3,C8–C12 rings with distance of 3.647 Å and angle of 72.53°; other stacking as C(4)–H(10a)/N3,C8–C12 with distance of 3.521 Å

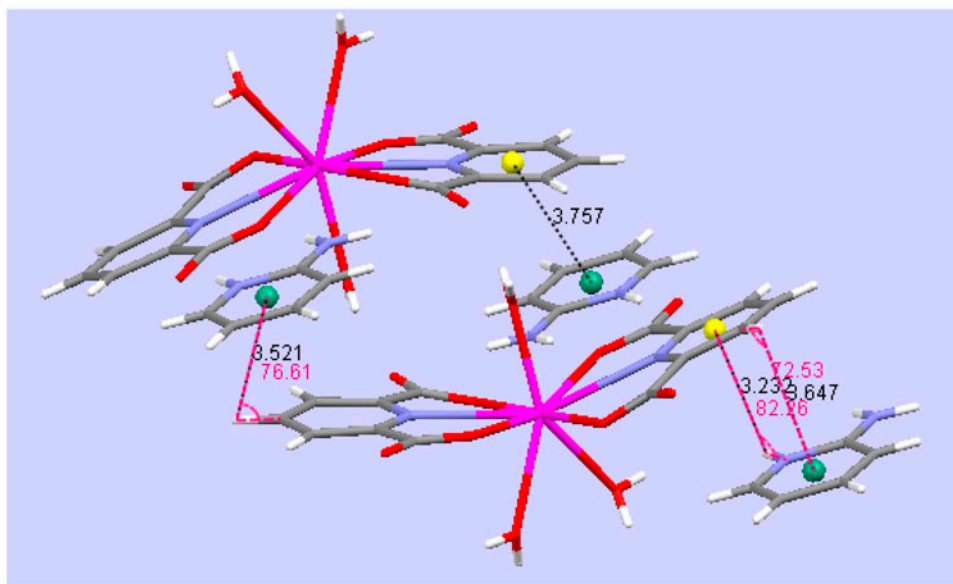


Figure 13. N-H $\cdots\pi$, C-H $\cdots\pi$ and $\pi\cdots\pi$ interactions in **2**.

and angle of 76.61° is shown in figure 13. Also, $\pi\cdots\pi$ stacking interactions between N1, C2–C6 ring and N3, C8–C12 have distance of 3.757 \AA .

3.2.2. Description of noncovalent interactions in $(2\text{-apyH})_2[\text{Ba}(\text{pydc})_2(\text{H}_2\text{O})_3]\cdot 5\text{H}_2\text{O}$ (**3**).

In **3**, intermolecular interactions, such as hydrogen bonding (O–H \cdots O, N–H \cdots O, C–H \cdots O), π stacking (C–O $\cdots\pi$, C–H $\cdots\pi$, N–H $\cdots\pi$ and π – π), electrostatic attraction between ion pairs, and donor-acceptor interactions, may result in self-association or self-assembly.

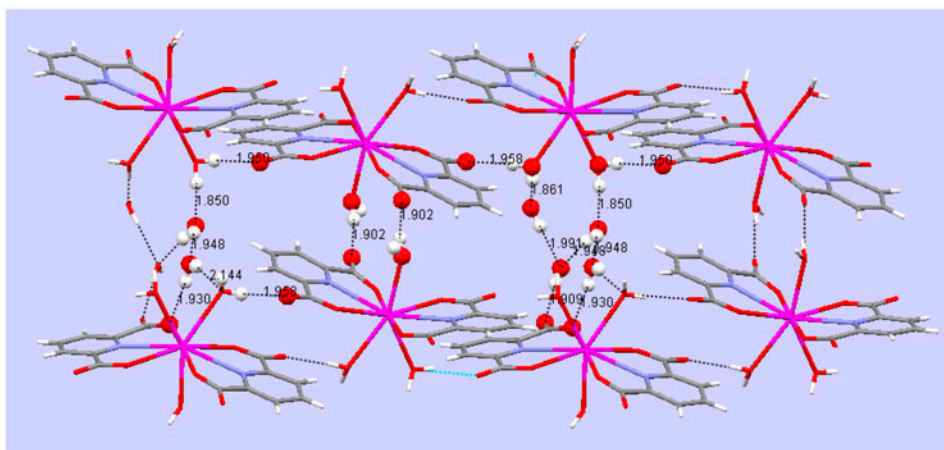


Figure 14. Complicated hydrogen bond network in different directions in **3**.

In the structure of **3**, the network of intra and intermolecular hydrogen bonds with D...A distances ranging from 2.674(5) to 3.497(5) Å (table 6) causes further stabilization for crystalline graph set descriptors that are formed in different directions, as shown in figure 14.

The π stacking interactions that can be observed in this structure are between C14–O15/N5', C6'–C10' ring with distance of 3.961 Å and angle of 109.30°, C9'–H9'/N1K, C2K–C6K ring with distance of 3.199 Å and angle of 87.34°, N1L–H1L/N5, C6–C10 ring with distance of 3.289 Å and angle of 79.26° and π – π stacking between N1L, C2L–C6L/N5, C6–C10 rings with distance of 3.620 Å (figure 15).

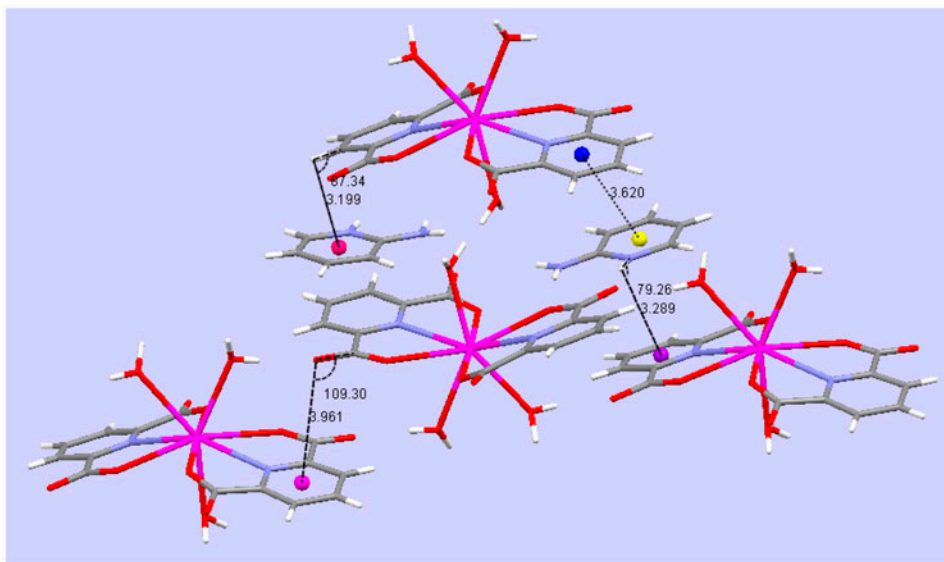


Figure 15. C–O... π , C–H... π , N–H... π and π ... π interactions in **3**.

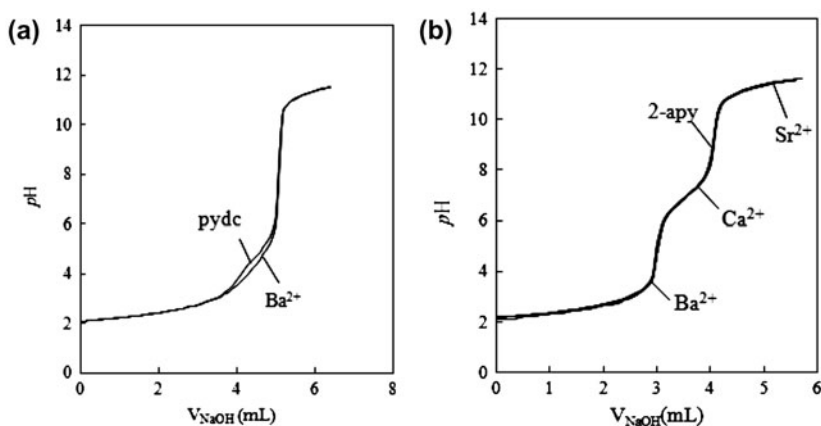


Figure 16. Potentiometric titration curves of pydc (a) in the absence and presence of Ba^{2+} and 2-apy (b) in the absence and presence of M^{2+} ions with NaOH 0.0983 M in aqueous solution at 25 °C and $\mu = 0.1$ M KNO_3 ; M = Sr^{2+} , Ca^{2+} and Ba^{2+} .

3.3. IR Studies of 1–3

The IR spectroscopy has been widely used for investigation of metal-organic complexes. The most definitive features in the IR spectra are the loss of the broad carboxylic acid O–H stretch together with the presence of asymmetric and symmetric carboxylate stretches. The IR spectra contained several absorptions at 1650–1665 cm^{-1} for stretching vibration of C=O pyridine-2,6-dicarboxylate. The strong absorptions at 1073 and 1105 cm^{-1} are assigned to C–O and C–N, respectively. The stretching frequencies of C=C aromatic rings appeared at 1378 and 1366 cm^{-1} . Furthermore, stretching and bending frequencies of C–H aromatic rings are assigned at 3054–3089 and 746–914 cm^{-1} , respectively. Lattice water normally appears at 2339–3460 cm^{-1} (antisymmetric and symmetric OH stretching) and 1620 cm^{-1} (HOH bending). The strong broad peaks at 3397–3492 cm^{-1} are attributed to N–H stretch coupled with hydrogen bonding between water molecules.

3.4. Potentiometric studies

The fully protonated forms of pydc (L) and 2-apy (Q) were titrated with a standard NaOH solution to obtain some information about their protonation constants as the components of the pydc-2-apy adduct system. The protonation constants of pydc [37, 48, 55] and 2-apy [55] were calculated by fitting the volume-pH data to the BEST program.

Evaluation of the equilibrium constants for the interaction between pydc and 2-apy in different protonation forms was accomplished through comparison of the calculated and experimental pH profiles [37, 38, 56], obtained with both pydc and 2-apy present. The results are reported in our previous article [55].

To evaluate the stoichiometry and stability of Ca^{2+} , Sr^{2+} , and Ba^{2+} complexes with pydc-2-apy adduct system in aqueous solution, the equilibrium potentiometric pH titration profiles of pydc [48], 2-apy and their 1 : 1 mixture were obtained in the absence and presence

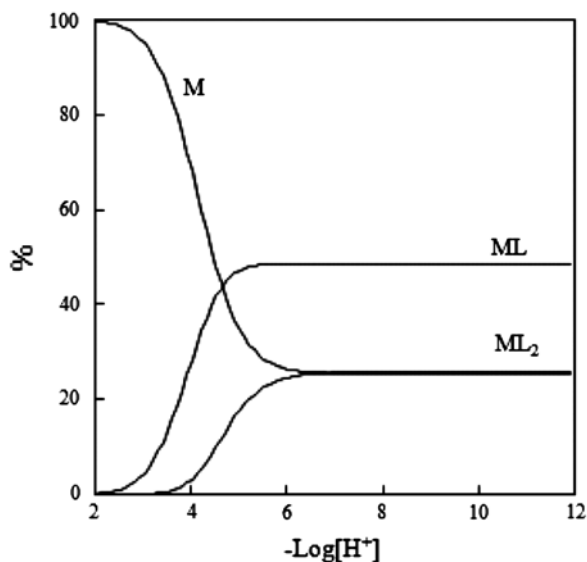


Figure 17. Distribution diagrams of pydc (L)/ Ba^{2+} binary systems.

Table 7. Overall stability constants of 2-apy/pydc/M²⁺ (q/l/m) binary and ternary systems in aqueous solution at 25 °C and $\mu = 0.1$ M KNO₃.

System	m	l	q	h	Log β	Max. %	at pH
Ca-pydc-2-apy	1	1	1	1	12.15	5.16	5.1
	1	1	1	2	17.84	96.0	2.0
Ba-pydc	1	1	0	0	3.19	48.6	>5.5
	1	2	0	0	5.51	25.6	>6.9
Ba-pydc-2-apy	1	1	1	1	8.22	Negligible	–
	1	1	1	2	12.50	Negligible	–
	1	1	1	3	16.61	45.6	6.2
Sr-pydc-2-apy	1	1	1	1	14.68	31.0	5.4
	1	1	1	3	21.62	69.8	2.0

of the cited ions. Information about pydc with Ca²⁺ and Sr²⁺ were reported previously [38, 57]. Titration of 2-apy (figure 16b) in the presence of metal ions stopped further formation of precipitate in the solution. It was found that there is no reaction between 2-apy and these

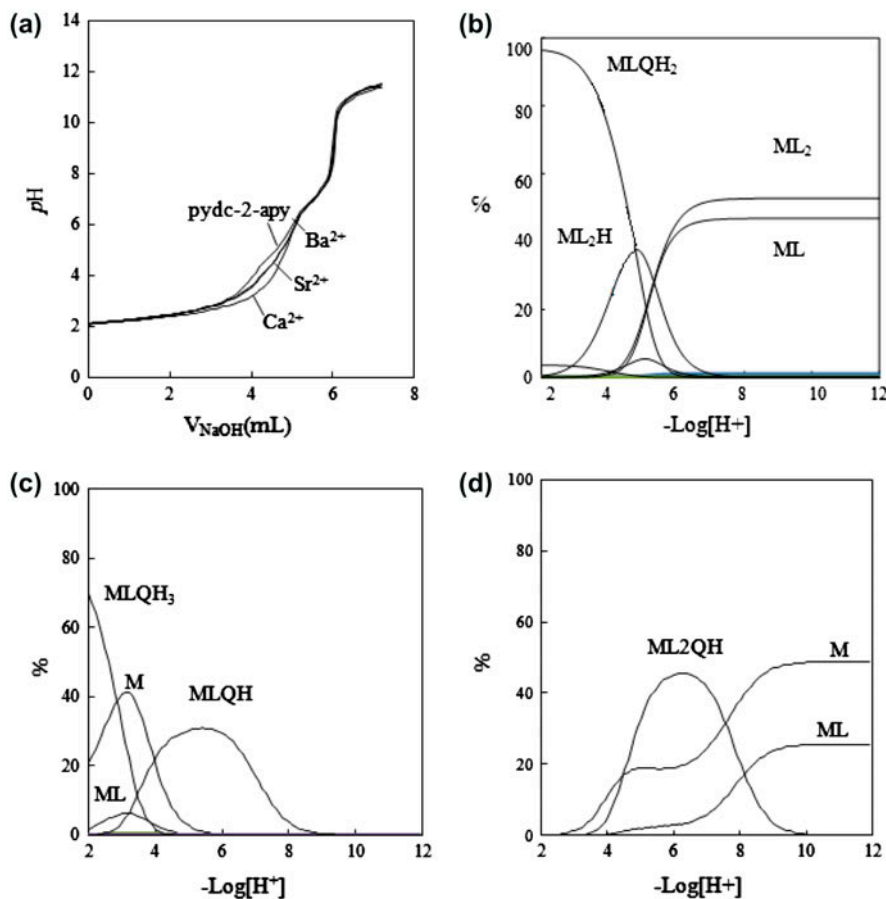


Figure 18. Potentiometric titration curves of pydc + 2-apy in the absence and presence of M²⁺ ions with NaOH 0.0983 M in aqueous solution at 25 °C and $\mu = 0.1$ M KNO₃, M = Ca²⁺, Sr²⁺ and Ba²⁺ (a) and distribution diagrams of pydc(L)/2-apy(Q)/M ternary systems. M = Ca²⁺ (b), Sr²⁺ (c) and Ba²⁺ (d).

metal ions. Figures 16(a) and 18(a) and our previous reports [38, 57] describe the relative weak interaction between pydc and pydc-2-apy with the cited metal ions.

The cumulative stability constants of $M_mL_lQ_qH_h$, β_{mlqh} , are defined in our previous publications [37, 48]. There are M, L, Q, and H as metal ion, pydc, 2-apy, 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 to the BEST program and the resulting values for the most likely complexed species in aqueous solutions are included in table 7 and the corresponding distribution diagrams are shown in figures 17 and 18. These results reveal that Ba^{2+} forms relatively weak complexes with pydc alone and pydc-2-apy systems, but no complex was observed between 2-apy and Ca^{2+} , Sr^{2+} , and Ba^{2+} .

As obvious from figure 17 and table 7 in the case of pydc(L), the most likely species for Ba^{2+} are BaL and BaL_2 . Figures 18(b)–(d), and table 7 reveal formation of a variety of ternary complexes between the above-mentioned cations and the adduct system at different ranges of pH. The predominant species for Ca^{2+} are: CaL (at pH 6.3), CaL_2 (at pH 6.2), $CaLQH$ (at pH 5.1), and $CaLQH_2$ (at pH 2.0); for Sr^{2+} : $SrLQH$ (at pH 5.4) and $SrLQH_3$ (at pH 2.0); for Ba^{2+} : $BaLQH_3$ (at pH 6.2). Stoichiometries of some of the most abundant ternary complexes, existing in aqueous solution, are very similar to those reported for the corresponding isolated complexes in the solid state.

4. Conclusion

Three supramolecular coordination compounds, $[Ca(pydc)(\mu-H_2O)(H_2O)_2]_n$, $(2-apyH)_2[Sr(pydc)_2(H_2O)_3] \cdot 5H_2O$, and $(2-apyH)_2[Ba(pydc)_2(H_2O)_3] \cdot 5H_2O$ (pydc = pyridine-2,6-dicarboxylate, 2-apy = 2-aminopyridine), were obtained by treatment of pyridine-2,6-dicarboxylic acid and 2-aminopyridine with the corresponding metal salts. Characterization was carried out using X-ray single crystal diffraction and potentiometric pH titration. The protonation constants of 2-apy and $pydcH_2$, the building blocks of the adduct system including pydc-2-apy fragment, and the corresponding stability constants of the system were determined. Hydrogen bonds, $N-H \cdots \pi$, $C-H \cdots \pi$, $C-O \cdots \pi$, and $\pi-\pi$ stacking interactions make a 3-D stable network. Results of solution studies confirmed the results of the solid state.

Supplementary material

Crystallographic data for these structures have been deposited with the Cambridge Crystallographic Data Center, CCDC 850101 for Sr(II), 850102 for Ba(II), and 850103 for Ca(II). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44(0) 1223336033; Email: deposit@ccdc.cam.ac.uk.

References

- [1] B.F. Hoskins, R. Robson. *J. Am. Chem. Soc.*, **112**, 1546 (1990).
- [2] T. Savaki, T. Dewa, Y. Aoyama. *J. Am. Chem. Soc.*, **120**, 8539 (1998).
- [3] K. Seki, S. Takamizawa, W. Mori. *Chem. Lett.*, **30**, 122 (2001).

- [4] H. Maas, A. Currao, G. Calzaferri. *Angew. Chem. Int. Ed.*, **41**, 2495 (2002).
- [5] H. Tsukube, S. Shinoda. *Chem. Rev.*, **102**, 2389 (2002).
- [6] M.L. Tong, X.M. Chen, S.R. Batten. *J. Am. Chem. Soc.*, **125**, 16170 (2003).
- [7] C.Y. Niu, B.L. Wu, X.F. Zheng, H.Y. Zhang, H.W. Hou, Y.Y. Niu, Z.J. Li. *Cryst. Growth Des.*, **8**, 1566 (2008).
- [8] J.B. English, A.E. Martell, R.J. Motekaitis, I. Murase. *Inorg. Chim. Acta*, **258**, 183 (1997).
- [9] J.P. Zhang, Y.Y. Lin, X.C. Huang, X.M. Chen. *J. Am. Chem. Soc.*, **127**, 5495 (2005).
- [10] M.H. Klingele, S. Brooker. *Coord. Chem. Rev.*, **241**, 119 (2003).
- [11] P.J. Rosado, K. Ruhlandt-Senge. *J. Coord. Chem.*, **64**, 186 (2011).
- [12] L.D. Wang, F. Tao, M.L. Cheng, Q. Liu, W. Han, Y.J. Wu, D.D. Yang, L.J. Wang. *J. Coord. Chem.*, **65**, 923 (2012).
- [13] X. Wang, L.K. San, H. Nguyen, N.M. Shafer, M.T. Hernandez, Z. Chen. *J. Coord. Chem.*, **66**, 826 (2013).
- [14] S.K. Seth, I. Saha, C. Estarellas, A. Frontera, T. Kar, S. Mukhopadhyay. *Cryst. Growth Des.*, **11**, 3250 (2011).
- [15] B. Sarma, N.K. Nath, B.R. Bhogala, A. Nangia. *Cryst. Growth Des.*, **9**, 1546 (2009).
- [16] A. Majumder, V. Gramlich, G.M. Rosair, S.R. Batten, J.D. Masuda, M.S. El Fallah, J. Ribas, J.P. Sutter, C. Desplanches, S. Mitra. *Cryst. Growth Des.*, **6**, 2355 (2006).
- [17] C. Hayes, K.C. Katz, M.A. Devane, J.G. Hsieh, J.T.C. Wolfe, D.L. Potter, P.J.A.R. Blight. *J. Clin. Pharmacol.*, **43**, 379 (2003).
- [18] H. Park, A.J. Lough, J.C. Kim, M.H. Jeong, Y.S. Kang. *Inorg. Chim. Acta*, **360**, 2819 (2007).
- [19] T. Douki, B. Setlow. *J. Photochem. Photobiol.*, **B**, **4**, 591 (2005).
- [20] K. Murakami, Y. Tanemura, M. Yoshino. *J. Nutr. Biochem.*, **14**, 99 (2003).
- [21] Y. Kazuhiro, Y. Noriko, F. Tadayasu. Eur. Patent EP0603165 (1994).
- [22] J.A. Burdock. *Encyclopedia of Food and Color Additives*, Vol. 3, CRC Press (1996).
- [23] J.R.H. Xie, V.H. Smith, R.E. Allen. *Chem. Phys.*, **322**, 254 (2006).
- [24] Z. Dega-Szafran, A. Kania, B. Nowak-Widra, M. Szafran. *J. Mol. Struct.*, **322**, 223 (1994).
- [25] R.K. Golder, C.M. Fitchett, J.L. Wikaira, P.J. Steel. *Acta Crystallogr. Sect. E: Struct.*, **Rep 66**, 1324 (2010).
- [26] H.K. Fun, A. Sinthya, S.R. Jebas, S. Devadasan. *Acta Crystallogr. Sect. E: Struct.*, **Rep 64**, 853 (2008).
- [27] P.A. Stabnikov, G.I. Zharkova, N.I. Alferova, A.P. Zubareva, E.A. Shusharina, N.V. Pervukhina. *J. Struct. Chem.*, **52**, 371 (2011).
- [28] B. Dojer, Z. Jaglicic, M. Kristl, M. Drogenik. *Monatsh. Chem.*, **143**, 73 (2011).
- [29] M.A. Ghandour, E.A. Aboul-kasim, A.H. Ameralla, N.A. Abdalla, O.A. Farghaly, Assiut University second pharmaceutical conference, Assiut, Egypt, pp. 115–123, 8–9 March (2000).
- [30] H.A. Mahamed, H.M.A. Wadood, O.A. Farghaly. *J. Pharm. Biomed. Anal.*, **28**, 819 (2002).
- [31] H. Park, A.J. Lough, J.C. Kim, M.H. Jeong, Y.S. Kang. *Inorg. Chim. Acta*, **360**, 2819 (2007).
- [32] J.R.H. Xie, V.H. Smith Jr, R.E. Allen. *Chem. Phys.*, **322**, 254 (2006).
- [33] M. Mirzaei, H. Eshtiagh-Hosseini, V. Lippolis, H. Aghabozorg, D. Kordestani, A. Shokrollahi, R. Aghaei, A.J. Blake. *Inorg. Chim. Acta*, **370**, 141 (2011).
- [34] K.M. Fromm. *Coord. Chem. Rev.*, **252**, 856 (2008).
- [35] H.C. Freeman. In *Inorganic Biochemistry*, J. Eichhorn (Ed.), Vol. 1, pp. 129–131. Marcel Dekker, New York, NY (1979).
- [36] J. Soleimannejad, H. Aghabozorg, M. Nasibipour, S. Najafi, F. Manteghi, A. Shokrollahi, E. Karami, M. Shamsipur. *J. Iran. Chem. Soc.*, **9**, 415 (2012).
- [37] A. Moghimi, S. Sheshmani, A. Shokrollahi, M. Shamsipur, G. Kickelbik, H. Aghabozorg. *Z. Anorg. Allg. Chem.*, **631**, 160 (2005).
- [38] H. Aghabozorg, F. Manteghi, M. Ghadermazi, M. Mirzaei, A.R. Salimi, A. Shokrollahi, S. Derki, H. Eshtiagh-Hosseini. *J. Mol. Struct.*, **919**, 381 (2009).
- [39] H. Aghabozorg, F. Ramezani-pour, J. Soleimannejad, M.A. Sharif, A. Shokrollahi, M. Shamsipur, A. Moghimi, J. Attar Gharamaleki, V. Lippolis, A.J. Blake. *Pol. J. Chem.*, **82**, 487 (2008).
- [40] A. Shokrollahi, M. Ghaedi, H.R. Rajabi, M.S. Niband. *Spectrochim. Acta, Part A*, **71**, 655 (2008).
- [41] H. Aghabozorg, F. Manteghi, S. Sheshmani. *J. Iran. Chem. Soc.*, **5**, 184 (2008).
- [42] H. Aghabozorg, E. Motieian, A.R. Salimi, M. Mirzaei, A. Shokrollahi, S. Derki, M. Ghadermazi, S. Sheshmani, H. Eshtiagh-Hosseini. *Polyhedron*, **29**, 1453 (2010).
- [43] H. Aghabozorg, S. Daneshvar, E. Motieian, F. Manteghi, R. Khadivi, M. Ghadermazi, A. Shokrollahi, M. Ghaedi, S. Derki, M. Shamsipur. *J. Iran. Chem. Soc.*, **6**, 620 (2009).
- [44] V.H. Rodrigues, M. Hakimi, E. Motieian. *Acta Crystallogr. Sect. E*, **68**, O1524 (2012).
- [45] H. Eshtiagh Hosseini, A. Hassanpoor, N. Alfi, M. Mirzaei, K.M. Fromm, A. Shokrollahi, F. Gschwindz, E. Karami. *J. Coord. Chem.*, **63**, 3175 (2010).
- [46] G.M. Sheldrick. *SADABS*, University of Gttingen, Germany (1996).
- [47] G.M. Sheldrick. *SHELXS97 and SHELXL97*, University of Gttingen, Germany (1997).
- [48] H. Aghabozorg, F. Ramezani-pour, P.D. Kheirollahi, A.A. Saei, A. Shokrollahi, M. Shamsipur, F. Manteghi, J. Soleimannejad, M.A. Sharif. *Z. Anorg. Allg. Chem.*, **632**, 147 (2006).
- [49] Z. Aghajani, H. Aghabozorg, E. Sadr-Khanlou, A. Shokrollahi, S. Derki, M. Shamsipur. *J. Iran. Chem. Soc.*, **6**, 373 (2009).

- [50] F. Ramezanipour, H. Aghabozorg, A. Shokrollahi, M. Shamsipur, H. Stoeckli-Evans, J. Soleimannejad, S. Sheshmani. *J. Mol. Struct.*, **779**, 77 (2005).
- [51] A.E. Martell, R.J. Motekaitis. *Determination and Use of Stability Constants*, 2nd Edn, VCH, New York, NY (1992).
- [52] L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabantini, A. Vacca. *Coord. Chem. Rev.*, **184**, 311 (1999).
- [53] M.C. Etter, J.C. Mac Donald, J. Bernstein. *Acta Cryst.*, **B46**, 256 (1990).
- [54] G.R. Desiraju, T. Steiner. *The Weak Hydrogen Bonds in Structural Chemistry and Biology*, Oxford University Press, Oxford (1999).
- [55] M. Mirzaei, H. Eshtiagh-Hosseini, N. Alfi, H. Aghabozorg, J. Attar Gharamaleki, S.A. Beyramabadi, H.R. Khavasi, A.R. Salimi, A. Shokrollahi, R. Aghaei, E. Karami. *J. Struct. Chem.*, **22**, 1365 (2011).
- [56] J.B. English, A.E. Martell, R.J. Motekaitis, I. Murase. *Inorg. Chim. Acta*, **258**, 183 (1997).
- [57] H. Aghabozorg, N. Firoozi, L. Roshan, M. Mirzaei, A. Shokrollahi, R. Aghaei, Z. Aghlmandi. *Iran. J. Chem. Eng.*, **30**, (2011).