

X-Ray, Crystal Structure and Solution Phase Studies of a Polymeric Sr^{II} Compound

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ABSTRACT: In the crystal structure of the title polymeric compound, $[C_{42}H_{38}N_6O_{33}Sr_5 \cdot 2(H_2O)]_n$, five independent metal atoms (Sr1-Sr5) have different coordination environments. The Sr1 and Sr5 atoms are nine coordinated and feature distorted tricapped trigonal-prismatic and capped square-antiprismatic geometries, respectively. The rest Sr^{II} atoms have eight coordination numbers. These units are connected via the carboxylate O atoms of mono- and di anionic forms of pyridine-2,6-dicarboxylic acid, (pydcH₂), and bridging water molecules that resulted in the formation of polymeric layers in 3-D. In the crystal structure, non-covalent interactions consisting of hydrogen bonds (O—H...O and C—H...O), π — π [interplanar distances of 3.413(2); 3.601(2) Å] and C=O... π [O... π distances of 3.249(3); 3.275(3) Å] stacking interactions play an important roles in stabilizing the structure. The protonation constants of propane-1, 2-diamine (1, 2-pn) and pyridine-2,6-dicarboxylate ion (pydc)²⁻, the equilibrium constants for the pydc-1,2-pn proton transfer system and the stoichiometry and stability of this system with Sr²⁺ ion in aqueous solution were investigated by potentiometric pH titrations. The stoichiometry of one of the most abundant complexed species in solution was found to be the same as that of the crystalline Sr^{II} complex.

KEY WORDS: Crystal structure, Sr^{II} complex, Hydrogen bonding, π — π interactions, C—H... π , and C=O... π stacking interactions.

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1021-9986/11/4/1

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INTRODUCTION

Metal-based coordination polymers have been extensively studied due to their intriguing topological structures [1-3] and unique functions, such as ion-exchange, adsorption, separation, sensor, and molecular recognition [4]. In this regard, the rational design and construction of coordination polymers with unique structural motifs and unique chemical and physical properties have attracted extensive interest in supramolecular chemistry and materials chemistry [5]. The framework structure of the coordination polymers is primarily dependent upon the coordination preferences of the central metal ions and the functionality of the ligands. Aside from the coordination bonding interactions, the hydrogen bonding and π - π stacking interactions, the solvent molecules, counter-ions and the ratio of metal salt to organic ligand also influence the formation of the ultimate architectures [6-10].

We have recently reported a proton transfer system, prepared using pyridine-2,6-dicarboxylic acid and propane-1,3-diamine $(\text{pnH}_2)(\text{pydcH})_2 \cdot 2(\text{pydcH}_2) \cdot 8\text{H}_2\text{O}$ and $(\text{pnH}_2)(\text{pydc}) \cdot (\text{pydcH}_2) \cdot 2.5\text{H}_2\text{O}$ [11,12]. Also complexes of Sr^{II} with pyridine-2,6-dicarboxylic acid $[\text{Sr}(\text{C}_7\text{H}_3\text{NO}_4) \cdot 4\text{H}_2\text{O}]$ and $[\text{Sr}(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_4]_n$ and $(\text{C}_{10}\text{H}_{10}\text{N}_2)[\text{Sr}(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ have been reported [13-15]. We have recently reported a proton transfer system, prepared using pyridine-2,6-dicarboxylic acid and propane-1,3-diamine $(\text{pnH}_2)(\text{pydcH})_2 \cdot 2(\text{pydcH}_2) \cdot 8\text{H}_2\text{O}$ and $(\text{pnH}_2)(\text{pydc}) \cdot (\text{pydcH}_2) \cdot 2.5\text{H}_2\text{O}$ [11,12]. Also complexes of Sr^{II} with pyridine-2,6-dicarboxylic acid $[\text{Sr}(\text{C}_7\text{H}_3\text{NO}_4) \cdot 4\text{H}_2\text{O}]$ and $[\text{Sr}(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_4]_n$ and $(\text{C}_{10}\text{H}_{10}\text{N}_2)[\text{Sr}(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ have been reported [13-15]. Recently, a novel cocrystal compound in the 2:1 stoichiometric ratio of 6-methyluracil (6mu) and pydcH_2 formulated as $[\text{6mu}]_2[\text{pydcH}_2]$, for the first time [16]. PydcH_2 which is incorporated in many biologically important systems, are subject of many experimental or/and theoretical studies. It is the body's prime natural chelator of vital trace elements: chromium, zinc, manganese, copper, iron and molybdenum. 6mu is a common and naturally occurring uracil derivative. Uracil itself has also very important roles in many biological processes. In this study for better understand of coordination behavior of this ligand, we planned a reaction in which pydcH_2 molecules self-assemble with Sr^{II} atoms affording crystals with a polymeric structural motif.

EXPERIMENTAL SECTION

Synthesis of the title polymeric compound, $[\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{33}\text{Sr}_5 \cdot 2(\text{H}_2\text{O})]_n$

The title compound was prepared by the reaction of 1,2-pn, (241 mg, 1 mmol), pydcH_2 , (380 mg, 2 mmol) and $\text{Sr}(\text{NO}_3)_2$ (241 mg, 2 mmol), in water (20 ml) in a 1:2:2 molar ratios, respectively. Colorless crystals were obtained by slow evaporation of the solvent at room temperature.

The X-ray data was collected on a Bruker SMART APEX II CCD Area Detector (MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$) at 100 K. The crystal data and experimental parameters are given in Table 1. The crystal was solved by direct methods (SHELXS-97) and a refinement was carried out with full-matrix least-squares methods based on F^2 with SHELXL-97 [17,18].

Solution studies equipment

A 794 Metrohm Basic Titrino Model 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 (home made thermostat), equipped with a stirrer and a 10.000-mL-capacity Metrohm piston burette. The pH meter-electrode system was calibrated to read $-\log [\text{H}^+]$.

Solution studies procedure

The details are described in references [19, 20]. The concentrations of 1,2-pn and pydc were $2.50 \times 10^{-3} \text{ M}$, for the potentiometric pH titrations of pydc , 1,2-pn and $\text{pydc} + 1,2\text{-pn}$, in the absence and presence of $1.25 \times 10^{-3} \text{ Sr}^{2+}$ ion. A standard carbonate-free NaOH solution (0.105 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. Ligands' protonation constants and stability constants of proton transfer and their metal complexes were evaluated using the BEST program described by Martell and Motekaitis [21]. The value of $K_w = [\text{H}^+][\text{OH}^-]$ used in the calculations according our previous works.

RESULTS AND DISCUSSION

The crystal structure of the title polymeric compound, $[\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{33}\text{Sr}_5 \cdot 2(\text{H}_2\text{O})]_n$, is presented in Fig. 1. The selected bond lengths are presented in Table 2.

Table 1: Crystallographic data for $[C_{42}H_{38}N_6O_{33}Sr_5 \cdot 2(H_2O)]_n$

| | |
|--|-----------------------------|
| Formula = $C_{42}H_{38}N_6O_{33}Sr_5 \cdot 2(H_2O)$ | |
| Formula weight = 1628.92 | |
| Crystal system = Monoclinic | $T = 100(2)$ K |
| Space group = Pn | $Z = 2$ |
| $a = 14.0874(4)$ Å | |
| $b = 6.8492(2)$ Å | $\beta = 97.4530(10)^\circ$ |
| $c = 28.0545(8)$ Å | |
| $V = 2684.04(13)$ Å ³ | |
| Absorption coefficient = 5.05 mm^{-1} | |
| $F(000) = 1612$ | |
| Crystal dimensions (mm) = $0.25 \times 0.14 \times 0.12$ | |
| $R[F^2 > 2\sigma(F^2)] = 0.034$ | |
| $R_{\text{int}} = 0.044$ | |
| Absorption Correction $T_{\text{min}}, T_{\text{max}}$ | Multi-scan 0.302, 0.547 |
| $R_w(F^2) = 0.063$ | $-19 \leq h \leq 19$ |
| θ range for data collection = 2.79 to 31.65° | $-9 \leq k \leq 9$ |
| Goodness to fit = 0.98 | $-39 \leq l \leq 39$ |
| $\Delta\rho_{\text{max}} = 0.64 \text{ e } \text{Å}^{-3}$ | |
| $\Delta\rho_{\text{min}} = -0.50 \text{ e } \text{Å}^{-3}$ | |
| Data collection = Bruker SMART APEX II CCD Area Detector | |
| Absorption correction: APEX2 | |
| No. of measured reflections = 33930 | |
| No. of independent reflections = 15483 | |
| No. of reflections collected with $I > 2\sigma(I) = 13553$ | |
| No. of parameters = 794 | |
| Structural determination = SHELXL-97 | |
| Refinement = full-matrix least-squares methods based on F^2 | |
| CCDC Number: Crystallographic data for this structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC number 787053. 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 deposition: deposit@ccdc.cam.ac.uk). | |

Table 2: Selected bond lengths (Å) for $[C_{42}H_{38}N_6O_{33}Sr_5 \cdot 2(H_2O)]_n$

| | | | |
|---------|-----------|-----------------------|-----------|
| Sr1—O1 | 2.646 (2) | Sr1—O27 | 2.609 (2) |
| Sr1—O3 | 2.591 (3) | Sr1—O17 ⁱ | 2.686 (3) |
| Sr1—O7 | 2.698 (2) | Sr1—O18 ⁱ | 2.957 (3) |
| Sr1—O25 | 2.603 (3) | | |
| | | | |
| Sr2—N2 | 2.648 (3) | Sr2—O28 | 2.694 (3) |
| Sr2—O3 | 2.485 (3) | Sr2—O29 | 2.666 (3) |
| Sr2—O5 | 2.626 (2) | Sr2—O16 ⁱⁱ | 2.478 (3) |
| Sr2—O7 | 2.745 (2) | Sr2—O22 ⁱ | 2.601 (3) |
| | | | |
| Sr3—N3 | 2.686 (3) | Sr3—O28 | 2.648 (3) |
| Sr3—O9 | 2.640 (2) | Sr3—O29 | 2.726 (2) |
| Sr3—O11 | 2.649 (3) | Sr3—O4 ⁱⁱⁱ | 2.500 (2) |
| Sr3—O15 | 2.509 (3) | Sr3—O20 | 2.628 (3) |
| | | | |
| Sr4—N4 | 2.659 (3) | Sr4—O30 | 2.606 (3) |
| Sr4—O13 | 2.640 (2) | Sr4—O31 | 2.576 (2) |
| Sr4—O15 | 2.578 (3) | Sr4—O32 | 2.587 (2) |
| Sr4—O11 | 2.591 (2) | Sr4—O23 | 2.679 (3) |
| | | | |
| Sr5—N5 | 2.710 (3) | Sr5—O23 | 2.655 (3) |
| Sr5—N6 | 2.710 (3) | Sr5—O12 | 2.689 (2) |
| Sr5—O17 | 2.537 (3) | Sr5—O33 | 2.654 (3) |
| Sr5—O19 | 2.785 (3) | Sr5—O8 ^{iv} | 2.619 (2) |
| Sr5—O21 | 2.704 (3) | | |

Symmetry codes: (i) $x-1/2, -y+1, z-1/2$; (ii) $x, y+1, z$; (iii) $x, y-1, z$; (iv) $x+1/2, -y+1, z+1/2$.

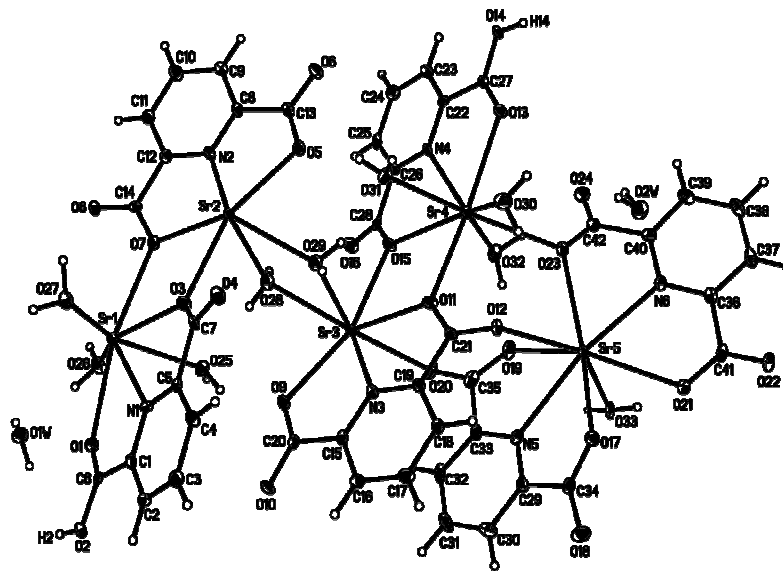
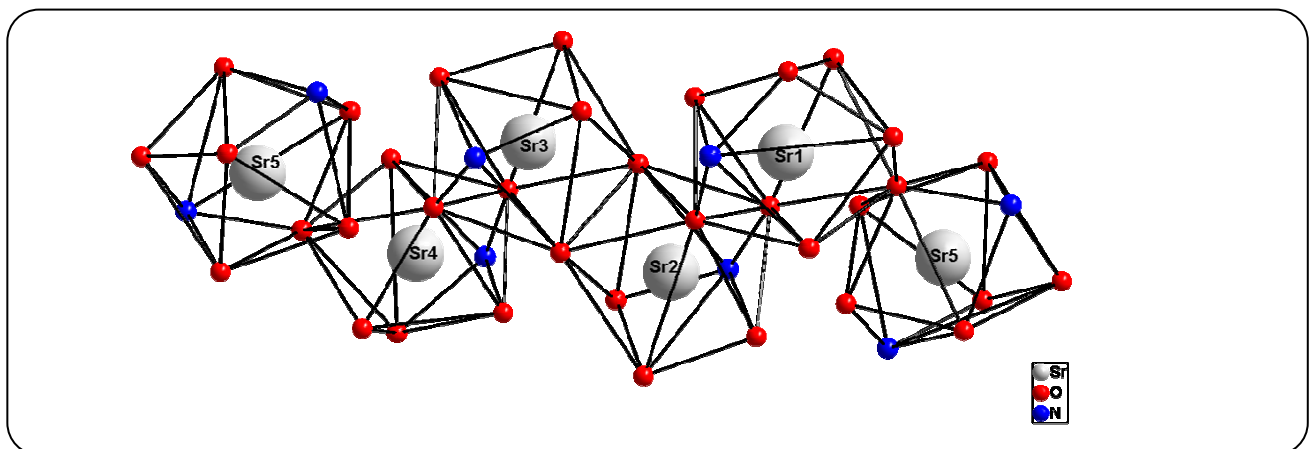


Fig. 1: Molecular Structure of the title polymeric compound, Independent part of unit cell, thermal ellipsoids are drawn at 50% probability level. Five independent metal atoms (Sr1-Sr5) have a different ligand environment: two of six ligand are protonated (O2 and O14), Sr2 and Sr3 are bridged two water molecules (O28 and O29), Sr5 chelated by two ligand, Sr1 and Sr5 have nine coordination state, the rest Sr atoms have eight coordination state.

Table 3: Selected Hydrogen bond geometry (\AA , $^\circ$) of $[\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{33}\text{Sr}_5\cdot 2(\text{H}_2\text{O})]_n$

| D—H...A | d(D—H) | d(H...A) | d(D...A) | $\angle(\text{D—H...A})$ |
|--------------------------------|--------|----------|-----------|--------------------------|
| O1W—H1WA...O18 ⁱ | 0.88 | 1.93 | 2.786 (4) | 164 |
| O1W—H1WB...O6 ^v | 0.83 | 2.15 | 2.900 (4) | 150 |
| O2W—H2WA...O10 ^{vi} | 0.86 | 2.57 | 3.263 (4) | 138 |
| O2W—H2WA...O13 ⁱⁱⁱ | 0.86 | 2.34 | 3.011 (4) | 135 |
| O2W—H2WB...O24 | 0.97 | 1.91 | 2.841 (4) | 160 |
| O2—H2...O6 ^v | 0.89 | 1.66 | 2.544 (4) | 174 |
| O14—H14...O10 ^{vii} | 0.91 | 1.57 | 2.469 (4) | 174 |
| O25—H25A...O9 | 0.87 | 2.01 | 2.787 (4) | 149 |
| O25—H25B...O27 ⁱⁱⁱ | 0.83 | 1.92 | 2.697 (4) | 155 |
| O26—H26A...O33 ^{viii} | 0.77 | 2.17 | 2.885 (4) | 155 |
| O26—H26B...O1W | 0.84 | 1.94 | 2.764 (4) | 167 |
| O27—H27A...O26 ⁱⁱ | 0.83 | 2.11 | 2.823 (4) | 143 |
| O27—H27B...O21 ⁱ | 0.99 | 1.66 | 2.650 (4) | 175 |
| O28—H28A...O22 ^{viii} | 0.79 | 2.09 | 2.846 (4) | 159 |
| O28—H28B...O25 | 0.79 | 2.00 | 2.782 (4) | 177 |
| O29—H29A...O31 | 0.80 | 2.00 | 2.760 (4) | 157 |
| O29—H29B...O20 ⁱⁱ | 0.85 | 2.11 | 2.943 (4) | 170 |
| O30—H30A...O12 | 0.85 | 2.31 | 2.935 (4) | 131 |
| O30—H30B...O2W ⁱⁱ | 0.83 | 2.00 | 2.824 (4) | 169 |
| O31—H31A...O5 | 0.93 | 1.85 | 2.746 (4) | 161 |
| O31—H31B...O32 ⁱⁱ | 0.82 | 1.88 | 2.667 (4) | 160 |
| O32—H32A...O24 | 0.86 | 2.05 | 2.868 (4) | 159 |
| O32—H32B...O19 | 0.85 | 1.92 | 2.737 (4) | 161 |
| O33—H33A...O12 ⁱⁱⁱ | 0.74 | 2.22 | 2.826 (4) | 139 |
| O33—H33B...O8 ^{ix} | 0.80 | 2.05 | 2.774 (4) | 151 |
| C3—H3A...O24 ^x | 0.95 | 2.41 | 3.103 (5) | 130 |
| C9—H9A...O1W ^{vii} | 0.95 | 2.48 | 3.399 (5) | 163 |
| C17—H17A...O1W ^{iv} | 0.95 | 2.52 | 3.295 (5) | 139 |
| C24—H24A...O1W ^{xi} | 0.95 | 2.49 | 3.323 (5) | 146 |

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

Fig. 2: Different coordination numbers around the central atoms in $[\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{33}\text{Sr}_5\cdot 2(\text{H}_2\text{O})]_n$.

Also hydrogen bond geometries are given separately in Table 3. This compound crystallized in the monoclinic system, space group Pn with two formula in the unit cell. The final R value was 0.034 for 33930 measured reflections.

According to the Fig. 1, five (Sr1-Sr5) atoms in the crystal structure have different coordination environments. The two Sr1 and Sr5 atoms are nine coordinated and feature distorted tricapped trigonal-prismatic and capped square-antiprismatic geometries, respectively (Fig. 2). The rest Sr^{II} atoms have eight coordination numbers. Indeed, the bridging role of the carboxylic group of (pydc)²⁻ ligand in the title polymer leads to a neutral complex which does not allow the propane-1,3-diaminium cation as a Lewis base to incorporate along the metallic complex and, thus, is crystallized in the produced network.

Sr2 and Sr3 atoms are bridged by two water molecules (O28 and O29), Sr5 is chelated by two (pydc)²⁻ ligands. Both *mono* and *di* anionic forms of the pyridine-2,6-dicarboxylic acid, (pydcH)⁻ and (pydc)²⁻, are seen in the crystal structure. These units are connected via the carboxylate O atoms of pyridine-2,6-dicarboxylic acid in order to form 3-D polymeric layers of the title compound. The range of Sr—O bond distances fall between 2.478(3) and 2.957(3) Å, and the mean Sr—N bond distance is 2.694 (3) Å.

The sum of O1—Sr1—O7, O1—Sr1—O27 and O7—Sr1—O27 bond angles for Sr1 equals to 359.83(8)° indicates that Sr1 atom is located in the center of O1O7O27 plane. For the Sr5 atom, the four O8, O12, O19 and N6 atoms form one square and O17, O21, O33 and N5 atoms create the second square which is twisted about 45 degrees respect to the first plane with a deviation of about 7 degrees, introducing square-antiprismatic geometry and O23 atom is located outside and forms a capped structure.

A noticeable feature of the title compound is the presence of C=O... π stacking interactions between C=O and aromatic rings of (pydc)²⁻ units. The O... π distances (measured to the centre of phenyl ring) are 3.275 (3) Å for C13=O6...Cg1 (x, y, z) and 3.249 (3) Å for C20=O10...Cg2 (x, y, z), [Cg1= N4/C22-C26 and Cg2= N1/C1-C5 rings].

Also a considerable π - π stacking interaction between aromatic rings of pyridine-2,6-dicarboxylate fragments with distances of 3.413(2) Å for Cg3...Cg4 (x, y, z) and

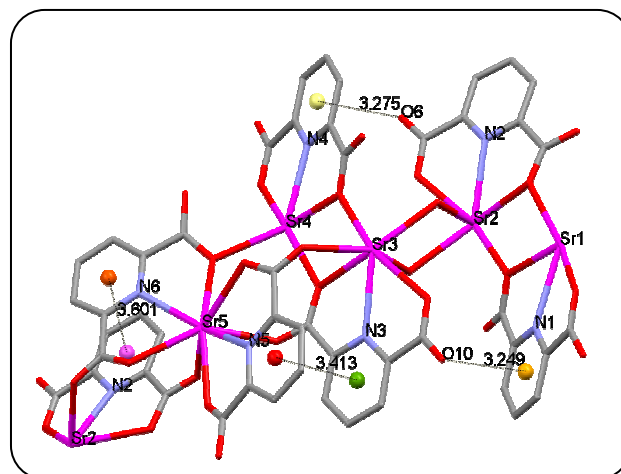


Fig. 3: C=O... π Stacking interactions between C=O and aromatic rings of (pydc)²⁻ units. O... π Distances are 3.275 (3) and 3.249 (3) Å. π - π Stacking interactions between aromatic rings of pyridine-2,6-dicarboxylate fragments with distances of 3.413(2) Å and 3.601(2) Å.

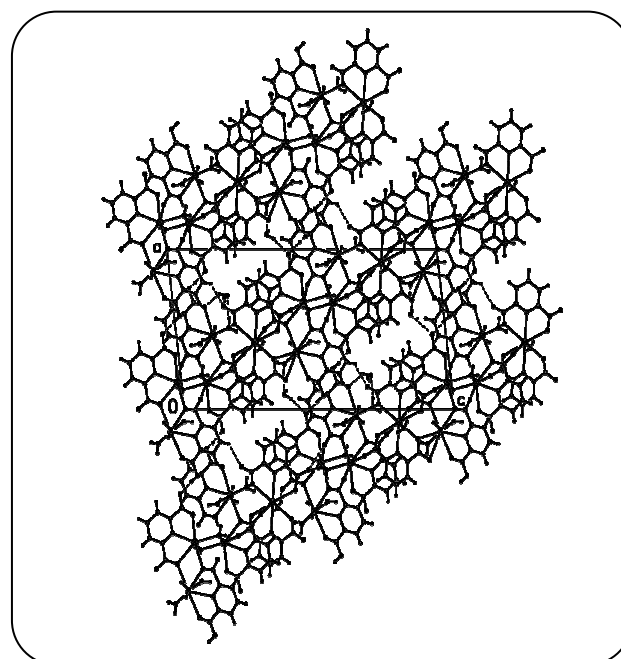


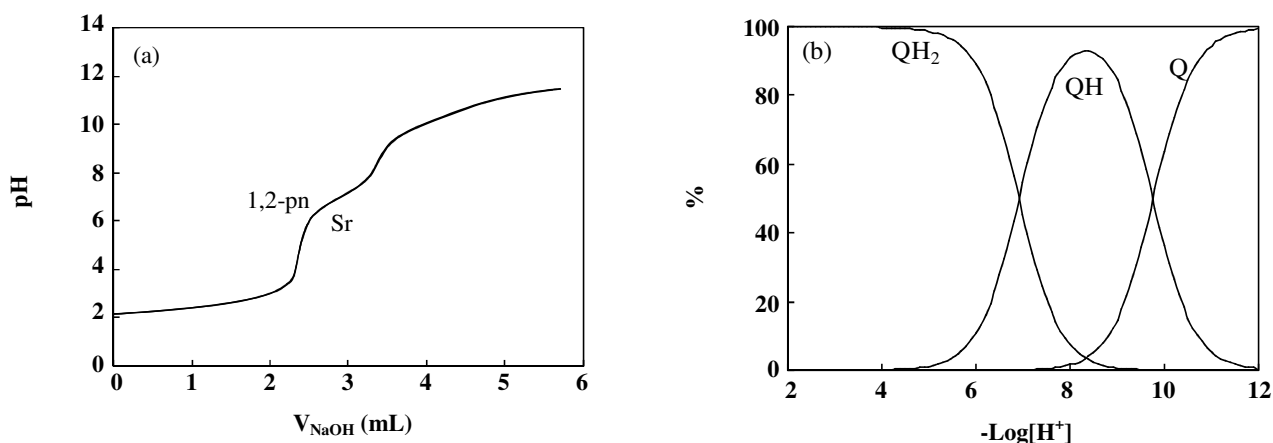
Fig. 4: Crystal Packing of the $[C_{42}H_{38}N_6O_{33}Sr_5 \cdot 2(H_2O)]_n$ along b crystal axis. Hydrogen bonds are shown as dashed lines.

3.601(2) Å for Cg5...Cg6 ($-1/2+x, 1-y, -1/2+z$) [Cg3, Cg4, Cg5 and Cg6 are centroids for N3/C15-C19, N5/C29-C33, N2/C8-C12 and N6/C36-C40 rings, respectively] are observed in the compound (Fig. 3).

There are a large number of O—H...O and C—H...O hydrogen bonds with distances ranging from 2.469(4) to 3.399(5) Å. The crystal packing diagram of the title

Table 4: Overall and stepwise protonation constants for pydc and 1,2-pn and recognition constants of interaction between them in 25 °C and $\mu = 0.1 \text{ M KNO}_3$.

| Stoichiometry | | | log β | Equilibrium quotient K | log K | max % | at pH |
|---------------|------|---|-------------|--|-------|-------|---------|
| 1,2-pn | pydc | h | | | | | |
| 0 | 1 | 1 | 5.08 | ----- | 5.08 | 93.9 | 3.6 |
| 0 | 1 | 2 | 7.20 | ----- | 2.12 | 55.9 | 2.0 |
| 1 | 0 | 1 | 9.75 | ----- | 9.75 | 92.8 | 8.3 |
| 1 | 0 | 2 | 16.67 | ----- | 6.92 | 99.9 | 2.0-3.9 |
| 1 | 1 | 1 | 11.96 | [1,2-pnpydcH]/[1,2-pnH][pydc] | 2.21 | 21.5 | 8.6 |
| 1 | 1 | 2 | 19.51 | [1,2-pnpydcH ₂]/[1,2-pnH][pydcH] | 4.68 | 42.7 | 5.9 |
| | | | | [1,2-pnpydcH ₂]/[1,2-pnH ₂][pydc] | 2.84 | | |
| 1 | 1 | 3 | 23.62 | [1,2-pnpydcH ₃]/[1,2-pnH ₂][pydcH] | 1.87 | 12.5 | 3.3 |

**Fig 5: Potentiometric titration curves for 1,2-pn in the absence and presence of Sr^{2+} ion with NaOH 0.105 M at 25 °C and $\mu=0.1 \text{ M KNO}_3$ (a) and distribution diagram of 1,2-pn(Q) (b).**

compound is shown along *b* crystal axis in Fig. 4, in which hydrogen bonds are presented by dashed lines. In comparison of van der Waals interactions presence in the crystalline network of the title polymeric compound on the basis of their strength the following series is derived: $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O} > \text{C}=\text{O}\cdots\pi > \pi-\pi$

In preliminary experiments, the fully protonated forms of pydc (L) and 1,2-pn (Q) were titrated with a standard NaOH aqueous solution (Fig. 5a), in order to obtain some information about their protonation constants as building blocks of the pydc-1,2-pn adduct.

The protonation constants of pydc [19, 20] and 1,2-pn were calculated by fitting the potentiometric pH data to

the BEST program The results are summarized in Table 4. It is noteworthy that the resulting log β values are in satisfactory agreement with those reported for 1,2-pn in the literature [22]. The evaluation of the equilibrium constants for the reactions of pydc with 1,2-pn in different protonation forms, was accomplished through comparison of the calculated and experimental pH profiles, obtained with both pydc and 1,2-pn present [23, 24]. The results are shown in Table 4. The corresponding species distribution diagrams for 1,2-pn and pydc-1,2-pn are shown in Figs. 5b and 6. It is obvious from these figures that the most abundant proton-transfer species present at pH 8.6 (21.5%), 5.9 (42.7%) and 3.3 (12.5%) are 1,2-pnHpydc

Table 5: Overall stability constants for 1,2-pn/ pydc/ Sr²⁺ binary and ternary systems at 25 °C and $\mu = 0.1$ M KNO₃.

| System | m | l | q | h | Log β | Max % | at pH |
|------------------|---|---|---|---|-------------|------------|---------|
| Sr - pydc | 1 | 1 | 0 | 0 | 5.61 | 70.2 | 5.0 |
| | 1 | 1 | 0 | 1 | 9.53 | 64.6 | 2.0 |
| | 1 | 2 | 0 | 0 | 8.43 | 34.8 | >7.8 |
| | 1 | 2 | 0 | 2 | 17.65 | 38.8 | 3.0 |
| Sr - pydc-1,2-pn | 1 | 1 | 1 | 1 | 17.51 | 15 | 8.4-8.7 |
| | 1 | 1 | 1 | 2 | 25.12 | 39.2 | 5.7 |
| | 1 | 2 | 1 | 2 | 26.59 | Negligible | ----- |
| | 1 | 2 | 1 | 3 | 33.32 | 22.8 | 4.3 |

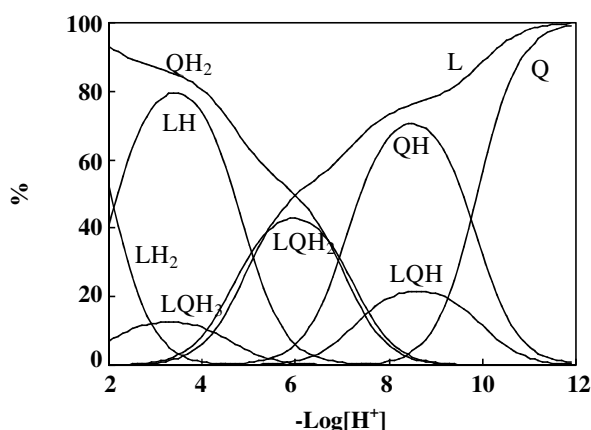


Fig. 6: Distribution diagram of proton transfer interaction between 1,2-pn (Q) and pydc (L).

(logK = 2.21), 1,2-pnH₂pydc (logK = 2.84) or 1,2-pnHpydcH (logK = 4.68) and 1,2-pnH₂pydcH (logK = 1.87). Thus, the solution studies provide additional evidence of association between 1,2-pn and pydc, supporting the evidence from the solid state studies.

In order to determine the stoichiometry and stability of the Sr²⁺ complexes with pydc-1,2-pn proton transfer system in aqueous solution, the equilibrium potentiometric pH titration profiles of 1,2-pn, pydc and their 1:1 mixture were obtained in the absence and presence of the Sr²⁺ ion (Figs. 5a, 7a and 8a). It was found for 1,2-pn-Sr system no

interaction between 1,2-pn and Sr²⁺ ion, while it was reported insignificant interaction between this ligands with some metal ions such as Cu²⁺, Ni²⁺, Hg²⁺, and Zn²⁺ in literature [22, 25-27]. As it is seen from Fig. 3a and 4a in the case of pydc and pydc-1,2pn relatively significant interaction with Sr²⁺ ion was observed.

The cumulative stability constants of M_mL_lQ_qH_h complexes β_{mlqh} , are defined in our previous publication [19, 20].

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 also included in Table 5.

The corresponding species distribution diagrams for pydc and pydc-1,2-pn in the presence of Sr²⁺ ions are shown in Figs. 7b and 8b. As it is seen from Table 5 and Fig. 7b for pydc-Sr system most likely binary species are: SrL, SrLH, SrL₂ and SrL₂H₂.

From Table 5 and Fig. 8b, it is readily seen that for the pydc-1,2-pn-Sr system, most likely ternary species are: SrLQH, SrLQH₂ and SrL₂QH₃, but in these systems, the binary species such as SrL, SrLH, SrL₂ and SrL₂H₂ are observed with high abundant. A comparisons between the stoichiometry of the crystalline complex and the observed binary species, clearly revealed that the crystalline complex structure possesses a stoichiometry with a coefficient of binary species.

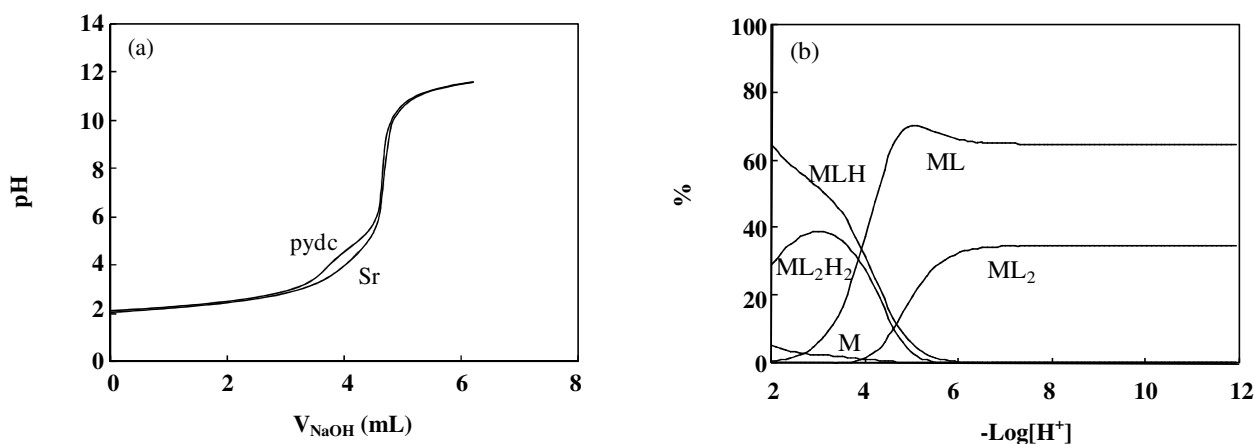


Fig. 7: Potentiometric titration curves for pydc in the absence and presence of Sr^{2+} ion with NaOH 0.105 M at 25 °C and $\mu=0.1$ M KNO_3 (a) and distribution diagram of pydc (L)/M binary system. $\text{M} = \text{Sr}^{2+}$ (b).

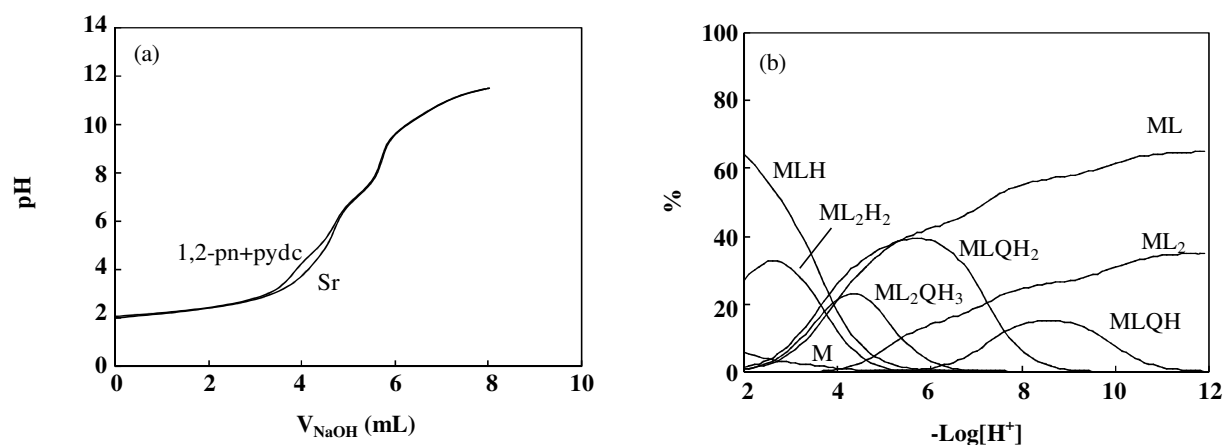


Fig. 8: Potentiometric titration curves for pydc+1,2-pn in the absence and presence of Sr^{2+} ion with NaOH 0.105 M at 25 °C and $\mu=0.1$ M KNO_3 (a), and distribution diagrams of pydc(L)/1,2-pn(Q)/M ternary systems. $\text{M} = \text{Sr}^{2+}$ (b).

CONCLUSIONS

In conclusion, it is clear that molecular polymer design, considering the many possible weak interactions as well as coordinative bonds, is imperative in crystal engineering of this category of compounds. In the crystal structure of the title polymeric compound, $[\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{33}\text{Sr}_5 \cdot 2(\text{H}_2\text{O})]_n$, there are five (Sr1-Sr5) atoms having different coordination environments. Comparing van der Waals interactions strength presence in the crystalline network of the polymeric compound on the following series may derive: $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O} > \text{C}=\text{O}\cdots\pi > \pi-\pi$. In order to determine the stoichiometry and stability of the Sr^{2+} complexes with pydc-1,2-pn, pydc and their 1:1 mixture were obtained in the absence

and presence of the Sr^{2+} ion. Results show the stoichiometry of one of the most abundant complexed species in solution was found to be same as that of the crystalline Sr^{II} complex. Further studies are in progress to prepare same complexes containing polycarboxylic ligands, for clarification of metal centre and/or ligands influence along with the van der Waals interaction in the final obtained coordination geometries [28].

Received : Aug. 5, 2010 ; Accepted : Mar. 7, 2011

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