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# A coordination polymer of Mn (III) with pyridine-2, 3-dicarboxylic acid and 4,4′-bipyridine

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**Abstract:** The polymeric compound, $\{(C_{10}H_9N_2)[Mn(C_7H_3NO_4)_2].(C_{10}H_8N_2).6H_2O\}_n$, was prepared by the reaction of manganese (II) nitrate with pyridine-2,3-dicarboxylic acid, (py-2,3-dc$H_2$) and 4,4'-bipyridine (4,4'-bipy) in a 1:2:4 molar ratio. The crystal system of the complex is monoclinic with space group $P2_1/n$ and four molecules per unit cell. The unit cell parameters are: a = 22.2099(15) Å, b = 6.6599(4) Å, c = 23.5921(16) Å and β = 104.014(3)°. The final R value was 0.04 based on 8960 reflections. The central atom is attached to two $(py\text{-}2,3\text{-}dc)^{2-}$ ligands through their N and O atoms in a planar square arrangement and two O atoms from bridging carboxylate groups, forming polymeric chains. So, the anionic complex features six-coordinate Mn (III) with a distorted octahedral geometry. In the crystal structure, a wide range of non-covalent interactions consisting of hydrogen bonding (of the types O−H···O, O−H···N and C−H···O), ion pairing, and π–π (centroid-centroid distances of 3.607 and 3.721 Å), C−H···π (with H···π distance of 2.941 Å) and C=O···π (with O···π distances of 2.943, 3.702 and 3.743 Å) stacking interactions stabilize the supramolecular structure.

**Keywords:** *Mn (III) complex; 4, 4'-bipyridine; crystal structure; hydrogen bonding.*

## 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 [4–7]. 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 [8–10]. 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.

The pyridinedicarboxylate ligands tend to be influenced by π-π interaction due to the presence of aromatic pyridine ring, favoring the formation of the orderly arrangement of the molecules. It is well known that carboxylate ligands play an important role in coordination chemistry and can adopt various binding modes such as terminal monodentate, chelating to one metal center, bridging bidentate to two metal centers, and bridging tridentate to two metal centers [11].

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Among pyridinedicarboxylic acids, py-2,3-dc$H_2$ is a good ligand for coordination and organic–inorganic hybrid compounds because of its flexible and varied coordination modes.

The rigid rod-like spacer molecules like 4,4'-bipyridine (4,4'-bipy) have been widely used as building blocks for the construction of metal–organic coordination frameworks [12]. The use of organic spacers, particularly flexible dicarboxylates bridging ligands and rigid planar bidentate diimines (4,4'-bipy) as building blocks to construct various metal assemblies is of growing interest in the field of molecular materials [11]. Recently, great success has been achieved by the combination of flexible aliphatic dicarboxylates and bipy as chelating bridging ligands, which resulted in compounds having 1–3D frameworks and unique physicochemical properties [13–15]. In this study, pyridine-2,3-dicarboxylic acids molecules (py-2,3-dc$H_2$) is coordinated to Mn(III) ions in presence of 4,4'-bipyridine (4,4'-bpy) and produced an anionic complex, this complex self-assembles with 4,4'-bipyridine (4,4'-bpy), protonated 4,4'-bipyridine (4,4'-bpy$H^+$) and water molecules affording a compound with a polymeric structural motif.

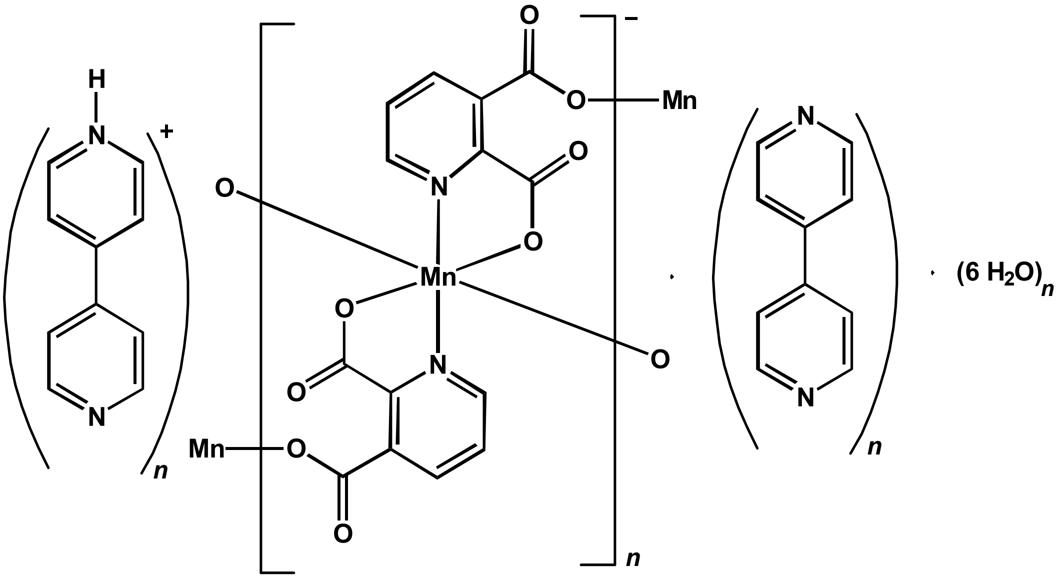
**Preparation and experiments:**

A solution of Mn $(NO_3)_2.6H_2O$ (143 mg, 0.5 mmol), pyridine-2,3-dicarboxylic acid (167 mg, 1 mmol) and 4,4′-bipyridine (312 mg, 2 mmol) in water (10 ml) was placed in autoclave and heated up to 120˚C for 2h (heating ramp 60˚C/h and cooling ramp 15˚C/h). Yellow crystals of the title polymeric compound were obtained after two weeks (yield 82%). Scheme 1 presents the chemical structure of the compound.

The x-ray data was collected on a Bruker SMART 1000 diffractometer ($MoK_\alpha$ radiation, $\lambda$ = 0.71073 Å) at 296 K.

**Results and discussion**

The molecular structure of the title polymeric compound is given in Figure 1. The crystal data and experimental parameters are depicted 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 [16] and the final atomic coordinates of non-hydrogen atoms and selected bond lengths and bond angles are presented in Tables 2 and 3, respectively. Also hydrogen bond geometries are given separately in Table 4. This compound crystallized in the monoclinic system, space group $P2_1/n$ with four formula units in the unit cell. The final R value was 0.04 for 8960 measured reflections.



Scheme 1

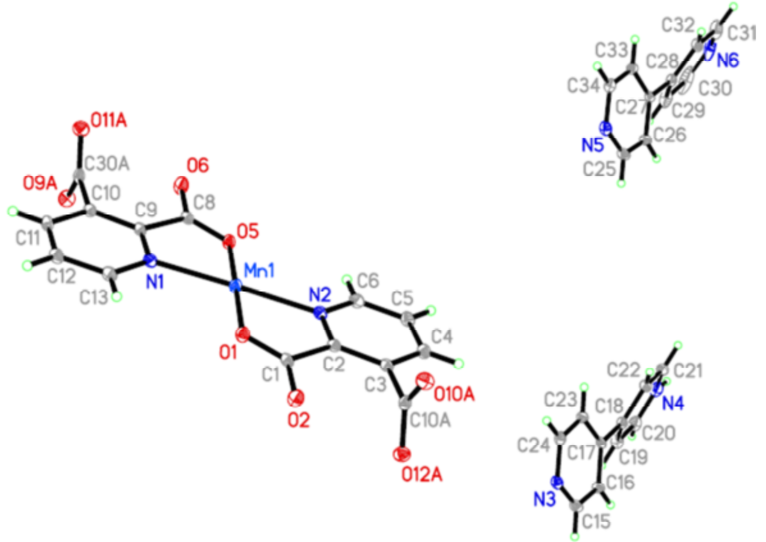


**Fig. 1** The molecular structure of the title compound, displacement ellipsoids are drawn at 50% probability level. Uncoordinated water molecules are omitted for clarity.

**Table 1.** Crystal and experimental data of the title compound

Formula = $C_{34}H_{35}MnN_6O_{14}$
Formula weight = 806.62
Crystal system = Monoclinic
$T = 296$ (2) K
Space group = $P2_1/n$
$Z = 4$
$a =$ 22.2099(15) Å
$b =$ 6.6599(4) Å
$\beta =$ 104.014(3)°
$c =$ 23.5921(16) Å
$V =$ 3385.8(4) Å$^3$
Absorption coefficient = 0.47 mm$^{-1}$
F(000) = 1672
Crystal dimensions (mm) = 0.38×0.32×0.29
$R[F^2 > 2\sigma(F^2)] = 0.04$
$R_{\text{int}} =$ 0.03
$R_w(F^2) = 0.127$
$-31 \leq h \leq 31$
θ range for data collection = 1.1 to 30.6 °
$-9 \leq k \leq 9$
Goodness to fit = 1.043
$-31 \leq l \leq 33$
$\Delta\rho_{\text{max}} =$ 1.48 e Å$^{-3}$
$\Delta\rho_{\text{min}} =$ -1.04 e Å$^{-3}$
Data collection = Bruker SMART 1000
Absorption correction: SADABS
No. of independent reflections = 10365
No. of reflections collected with $I > 2\sigma(I) =$ 8960
No. of parameters = 496
Program used to solve the structural = SHELXS-97
Program used to refine the structural = SHELXL-97

CCDC Number: Crystallographic data for this structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC number 778278. 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.** Atomic coordinate ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for non hydrogen atoms

| Atom | *x* | *y* | *z* | $U_{(eq)}$ |
|---|---|---|---|---|
| Mn1 | 0.245039 (9) | 0.00309 (3) | −0.002465 (8) | 0.01165 (7) |
| O1 | 0.29406 (5) | −0.20288 (15) | −0.04521 (4) | 0.01320 (18) |
| O1S | 0.81976 (5) | 0.22059 (16) | 0.77135 (4) | 0.0164 (2) |
| O2S | 0.14066 (5) | 0.47516 (16) | 0.14632 (4) | 0.0160 (2) |
| O2 | 0.36007 (5) | −0.46262 (17) | −0.03112 (4) | 0.0160 (2) |
| O3S | 0.17925 (5) | 0.74071 (16) | −0.27215 (5) | 0.0175 (2) |
| O4S | 0.35518 (5) | −0.44881 (17) | −0.14720 (4) | 0.0172 (2) |
| O5S | 0.78473 (5) | −0.14113 (17) | 0.80663 (5) | 0.0217 (2) |
| O5 | 0.19849 (5) | 0.21276 (15) | 0.04159 (4) | 0.01255 (18) |
| O6S | 0.21849 (6) | 0.38719 (17) | −0.30782 (5) | 0.0223 (2) |
| O6 | 0.13334 (5) | 0.47412 (17) | 0.02897 (5) | 0.0174 (2) |
| N1 | 0.21675 (5) | 0.25400 (17) | −0.06555 (5) | 0.0112 (2) |
| N2 | 0.27593 (5) | −0.24192 (17) | 0.06240 (5) | 0.0111 (2) |
| N3 | 0.55638 (6) | 0.08615 (18) | 0.71707 (5) | 0.0149 (2) |
| N4 | 0.45181 (6) | 0.1743 (2) | 0.97378 (6) | 0.0199 (3) |
| N5 | 0.05762 (6) | 0.10265 (19) | 0.71429 (5) | 0.0157 (2) |
| N6 | −0.06763 (10) | 0.1202 (3) | 0.96002 (8) | 0.0454 (6) |
| C1 | 0.32200 (6) | −0.3485 (2) | −0.01614 (5) | 0.0107 (2) |
| C2 | 0.30915 (6) | −0.38610 (19) | 0.04372 (5) | 0.0100 (2) |
| C3 | 0.33099 (6) | −0.5549 (2) | 0.07772 (6) | 0.0108 (2) |
| C4 | 0.31877 (6) | −0.5698 (2) | 0.13287 (6) | 0.0129 (2) |
| C5 | 0.28565 (6) | −0.4189 (2) | 0.15217 (6) | 0.0135 (2) |
| C6 | 0.26466 (6) | −0.2577 (2) | 0.11551 (6) | 0.0132 (2) |
| C8 | 0.17040 (6) | 0.3591 (2) | 0.01293 (5) | 0.0108 (2) |
| C9 | 0.18278 (6) | 0.39688 (19) | −0.04710 (5) | 0.0102 (2) |
| C10 | 0.16108 (6) | 0.5657 (2) | −0.08088 (5) | 0.0106 (2) |
| C11 | 0.17535 (6) | 0.5847 (2) | −0.13509 (6) | 0.0127 (2) |
| C12 | 0.21002 (6) | 0.4372 (2) | −0.15381 (6) | 0.0135 (2) |
| C13 | 0.22991 (6) | 0.2737 (2) | −0.11770 (6) | 0.0130 (2) |
| C15 | 0.59545 (7) | 0.0820 (2) | 0.77009 (6) | 0.0154 (3) |
| C16 | 0.57629 (6) | 0.0919 (2) | 0.82189 (6) | 0.0138 (2) |
| C17 | 0.51282 (6) | 0.10539 (19) | 0.81884 (6) | 0.0114 (2) |
| C18 | 0.49061 (6) | 0.1250 (2) | 0.87291 (6) | 0.0128 (2) |
| C19 | 0.52525 (7) | 0.2389 (2) | 0.91939 (6) | 0.0168 (3) |
| C20 | 0.50484 (7) | 0.2601 (2) | 0.96950 (7) | 0.0192 (3) |
| C21 | 0.41674 (7) | 0.0649 (2) | 0.93055 (7) | 0.0198 (3) |
| C22 | 0.43553 (7) | 0.0367 (2) | 0.87887 (7) | 0.0167 (3) |
| C23 | 0.47159 (6) | 0.1069 (2) | 0.76389 (6) | 0.0131 (2) |
| C24 | 0.49550 (7) | 0.0985 (2) | 0.71458 (6) | 0.0142 (2) |
| C25 | 0.09521 (7) | 0.1030 (2) | 0.76804 (6) | 0.0160 (3) |
| C26 | 0.07416 (6) | 0.1067 (2) | 0.81890 (6) | 0.0138 (2) |
| C27 | 0.01034 (6) | 0.10728 (19) | 0.81410 (6) | 0.0109 (2) |
| C28 | −0.01524 (6) | 0.1138 (2) | 0.86640 (6) | 0.0132 (2) |
| C29 | 0.01074 (9) | 0.2346 (2) | 0.91424 (7) | 0.0239 (3) |
| C30 | −0.01746 (13) | 0.2342 (3) | 0.96132 (8) | 0.0425 (6) |
| C31 | −0.09281 (10) | 0.0047 (3) | 0.91502 (10) | 0.0372 (5) |
| C32 | −0.06763 (7) | −0.0007 (2) | 0.86758 (8) | 0.0219 (3) |
| C33 | −0.02932 (6) | 0.1043 (2) | 0.75832 (6) | 0.0129 (2) |
| C34 | −0.00373 (7) | 0.1039 (2) | 0.71009 (6) | 0.0148 (2) |
| O10A | 0.33815 (5) | −0.86557 (16) | 0.03024 (5) | 0.0161 (2) |
| C10A | 0.36724 (6) | −0.7201 (2) | 0.05748 (6) | 0.0117 (2) |
| O12A | 0.42553 (5) | −0.70586 (16) | 0.07144 (4) | 0.01464 (19) |
| O9A | 0.15081 (5) | 0.87381 (16) | −0.03288 (5) | 0.0165 (2) |
| C30A | 0.12249 (6) | 0.7260 (2) | −0.06154 (6) | 0.0129 (2) |
| O11A | 0.06503 (5) | 0.70878 (16) | −0.07629 (4) | 0.0162 (2) |

**Table 3.** Selected bond distances (Å), and bond angels (°)

| | | | |
|---|---|---|---|
| Mn1−O1 | 2.1485 (10) | Mn1−N1 | 2.2247 (12) |
| Mn1−O5 | 2.1493 (10) | Mn1−N2 | 2.2285 (11) |
| Mn1−O10A$^{i}$ | 2.2056 (10) | Mn1−O9A$^{ii}$ | 2.2156 (11) |
| O1−Mn1−O5 | 178.36 (4) | O10A$^{i}$−Mn1−N1 | 91.44 (4) |
| O1−Mn1−O10A$^{i}$ | 83.03 (4) | O9A$^{ii}$−Mn1−N1 | 89.06 (4) |
| O5−Mn1−O10A$^{i}$ | 95.35 (4) | O1−Mn1−N2 | 75.41 (4) |
| O1−Mn1−O9A$^{ii}$ | 98.41 (4) | O5−Mn1−N2 | 104.35 (4) |
| O5−Mn1−O9A$^{ii}$ | 83.21 (4) | O10A$^{i}$−Mn1−N2 | 86.76 (4) |
| O10A$^{i}$−Mn1−O9A$^{ii}$ | 178.30 (4) | O9A$^{ii}$−Mn1−N2 | 92.72 (4) |
| O1−Mn1−N1 | 104.99 (4) | N1−Mn1−N2 | 178.10 (4) |
| O5−Mn1−N1 | 75.20 (4) | | |

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *y*−1, *z*.

**Table 4**. Hydrogen bond geometry (Å ,°)

| D−H···A | d(D−H) | d(H···A) | d(D···A) | <(D−H···A) |
|---|---|---|---|---|
| O1S−H1B···O2S$^{iii}$ | 0.85 | 1.96 | 2.7972 (15) | 170 |
| O1S−H1A···O5S | 0.85 | 1.88 | 2.7231 (15) | 173 |
| O2S−H2B···N3$^{iv}$ | 0.85 | 2.06 | 2.8229 (15) | 150 |
| O2S−H2A···O6 | 0.85 | 1.89 | 2.7338 (14) | 174 |
| O3S−H3B···O4S$^{v}$ | 0.85 | 1.95 | 2.7886 (15) | 168 |
| O3S−H3A···O6S | 0.85 | 1.87 | 2.7141 (16) | 171 |
| O4S−H4B···N5$^{vi}$ | 0.85 | 2.06 | 2.8032 (16) | 146 |
| O4S−H4A···O2 | 0.85 | 1.87 | 2.7159 (14) | 175 |
| O5S−H5B···O1S$^{vii}$ | 0.85 | 1.90 | 2.7479 (15) | 175 |
| O5S−H5A···O2S$^{viii}$ | 0.85 | 1.99 | 2.8348 (16) | 171 |
| O6S−H6B···O3S$^{ix}$ | 0.85 | 1.91 | 2.7558 (16) | 177 |
| O6S−H6A···O4S$^{x}$ | 0.85 | 1.98 | 2.8230 (16) | 170 |
| N4−H4C···O12A$^{xi}$ | 0.85 | 1.80 | 2.6339 (16) | 166 |
| N4−H4C···O10A$^{xi}$ | 0.85 | 2.55 | 3.1378 (17) | 127 |
| O1S−H1B···O2S$^{iii}$ | 0.85 | 1.96 | 2.7972 (15) | 170 |
| O1S−H1A···O5S | 0.85 | 1.88 | 2.7231 (15) | 173 |
| O2S−H2B···N3$^{iv}$ | 0.85 | 2.06 | 2.8229 (15) | 150 |
| O2S−H2A···O6 | 0.85 | 1.89 | 2.7338 (14) | 174 |
| O3S−H3B···O4S$^{v}$ | 0.85 | 1.95 | 2.7886 (15) | 168 |
| O3S−H3A···O6S | 0.85 | 1.87 | 2.7141 (16) | 171 |
| O4S−H4B···N5$^{vi}$ | 0.85 | 2.06 | 2.8032 (16) | 146 |
| O4S−H4A···O2 | 0.85 | 1.87 | 2.7159 (14) | 175 |
| O5S−H5B···O1S$^{vii}$ | 0.85 | 1.90 | 2.7479 (15) | 175 |
| O6S−H6B···O3S$^{ix}$ | 0.85 | 1.91 | 2.7558 (16) | 177 |
| O6S—H6A···O4S$^{x}$ | 0.85 | 1.98 | 2.8230 (16) | 170 |
| C13—H13···O6S$^{ix}$ | 0.93 | 2.58 | 3.4644 (18) | 160 |
| C20—H20···O2$^{viii}$ | 0.93 | 2.56 | 3.2897 (19) | 135 |
| C21—H21···O1$^{xii}$ | 0.93 | 2.50 | 3.4185 (19) | 169 |
| C24—H24···O11A$^{vi}$ | 0.93 | 2.44 | 3.2965 (17) | 153 |
| C31—H31···O5$^{xiii}$ | 0.93 | 2.27 | 3.133 (2) | 154 |
| C34—H34···O12A$^{xiv}$ | 0.93 | 2.45 | 3.3377 (17) | 159 |

**Symmetry codes:** (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*−1/2, −*y*+1/2, *z*−1/2; (v) −*x*+1/2, *y*+3/2, −*z*−1/2; (vi) −*x*+1/2, *y*−1/2, −*z*+1/2; (vii) −*x*+3/2, *y*−1/2, −*z*+3/2; (viii) −*x*+1, −*y*, −*z*+1; (ix) −*x*+1/2, *y*−1/2, −*z*−1/2; (x) −*x*+1/2, *y*+1/2, −*z*−1/2; (xi) *x*, *y*+1, *z*+1; (xii) *x*, *y*, *z*+1; (xiii) −*x*, −*y*, −*z*+1; (xiv) *x*−3/2, −*y*−3/2, *z*−1/2.

According to the crystal structure of the compound, the central atom is attached to two (py-2,3-dc)$^{2-}$ ligands through their N and O atoms in a planar square arrangement. Also, pyridine-2,3-dicarboxylate ligand, (py-2,3-dc)$^{2-}$, plays a bridging role. Its two carboxylic groups adopt monodentate coordination mode, one together with pyridine N atom coordinated to one Mn(III) ion, the other coordinates to second equivalent Mn(III) atom, forming polymeric chains.

In the compound, O9A and O10A atoms from bridging (py-2,3-dc)$^{2-}$ ligands [O10A$^{i}$−Mn1−O9A$^{ii}$ = 178.30 (4)°; i: x, y + 1, z, ii: x, y−1, z], and O1, O5, N1 and N2 atoms [N1−Mn1−N2 = 178.10(4)° and O1−Mn1−O5 = 178.36(4)°] are attached to the central atom. Therefore, the geometry of the resulting MnN$_2$O$_4$ coordination fragment can be described as slightly distorted octahedral.

The Mn1−O9$^{ii}$ and Mn1−O10$^{i}$ bonds [2.2156(11) and 2.2056(10) Å] are significantly longer than other Mn−O bonds [2.1485(10) and 2.1493(10) Å]. Also, the Mn−O bonds are almost perpendicular to the square plane and by connecting Mn (III) ions together result in the formation of polymeric chains along *b* direction. The metal-ligand bond distances are in agreement with published Mn (III) complexes [17,18]. There are also six uncoordinated water molecules, one neutral 4,4'-bipy molecule and one monoprotonated (4,4'-bipyH)$^{+}$ cation as counter-ion.

The two pyridine rings in the neutral 4,4'-bipy molecule and (4,4'-bipyH)$^{+}$ cation are twisted with respect to each other, making dihedral angles of 40.69(8) and 37.01(6)°, respectively.

A noticeable feature of the title compound is the presence of C=O···π stacking interactions between C=O groups of carboxylate groups with aromatic rings of (py-2,3-dc)− and (4,4'-bipyH)+ units. The C=O···π distances (measured to the center of phenyl ring) are 3.6986(12) Å for C1=O2···Cg1 (x, -1+y, z), 3.7017(13) Å for C8=O6···Cg2 (x, 1+y, z) and 3.7343(13) Å for C10A=O12A···Cg3 (1-x, -1-y, 1-z), [Cg1, Cg2 and Cg3 are the centroids for N1/C9-C13, N2/C2-C6 and N4/C18-C22 rings, respectively]. There is also an interesting C−H···π interaction between C29−H29···Cg3 and phenyl ring of (py-2,3-dc)$^{2-}$ unit with H···π distance of 2.94 Å (x, y, 1+z) (Fig. 2). Also a considerable π–π stacking interactions between aromatic rings of 4,4'-bipy and (4,4'-bipyH)$^{+}$ fragments with distances of 3.6065(8) and 3.7216(8) Å for Cg4···Cg5 (1/2-x, -1/2+y, 3/2-z) and (1/2-x, 1/2+y, 3/2-z) are observed in the prepared compound [Cg4 and Cg5 are centroids for N3/C15-C17,C23,C24 and N5/C25-C27,C33,C34 rings, respectively] (Fig.3) [19-23].

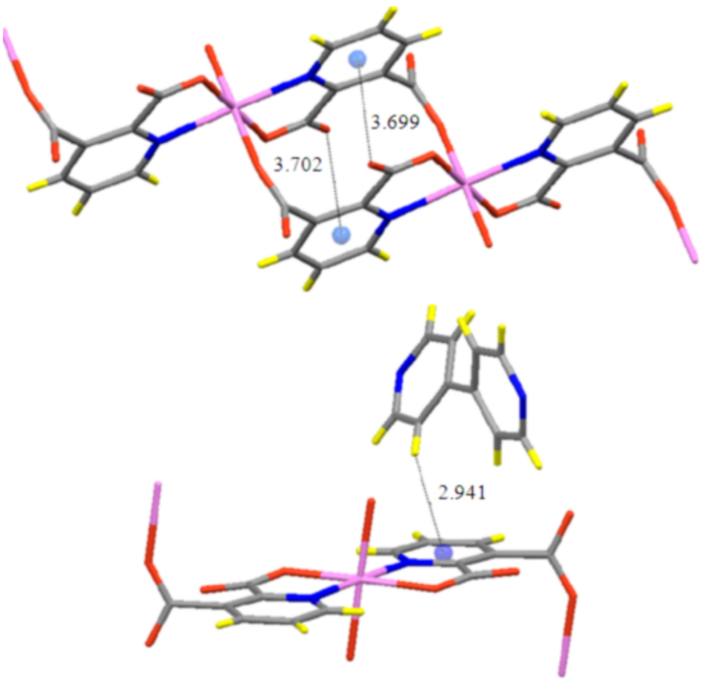


**Fig. 2** C=O···π and C−H··· π stacking interactions between C=O and C−H groups with aromatic rings of (py-2,3-dc)$^{2-}$ and (4,4'-bipyH)$^{+}$ units.

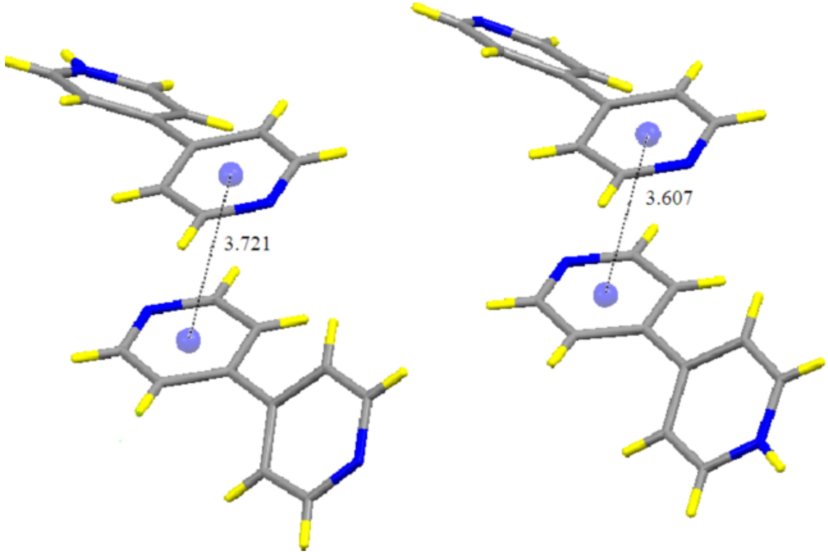


**Fig. 3** π–π stacking interactions between aromatic rings of 4,4'-bipy and $(4,4'\text{-bipyH})^+$ fragments with distances 3.6065(8) and 3.7216(8) Å for *Cg*4···*Cg*5 (1/2-*x*, -1/2 + *y*, 3/2-*z*) and (1/2-*x*, 1/2+*y*, 3/2-*z*) [*Cg*4 and *Cg*5 are the centroids for N3/C15-C17,C23,C24 and N5/C25-C27,C33,C34 rings, respectively].

As shown in Figure 4, in the crystal structure, a wide range of hydrogen bonding interactions consisting of O−H···O, O−H···N, N−H···O and C−H···O types with D···A ranging from 2.6339(16) to 3.4644(18) Å connect the different parts together to form layers in which the space between anionic chains is filled with cations and uncoordinated water molecules.

In addition, hydrogen bonds between water molecules create $(H_2O)_n$ clusters and these units connect the cations and anions together throughout the structure. These cyclic $(H_2O)_n$ clusters are shown at Figure 5 and are located in the space between layers of cations and anions. The crystal packing diagram of the polymeric compound is illustrated in Figure 6.

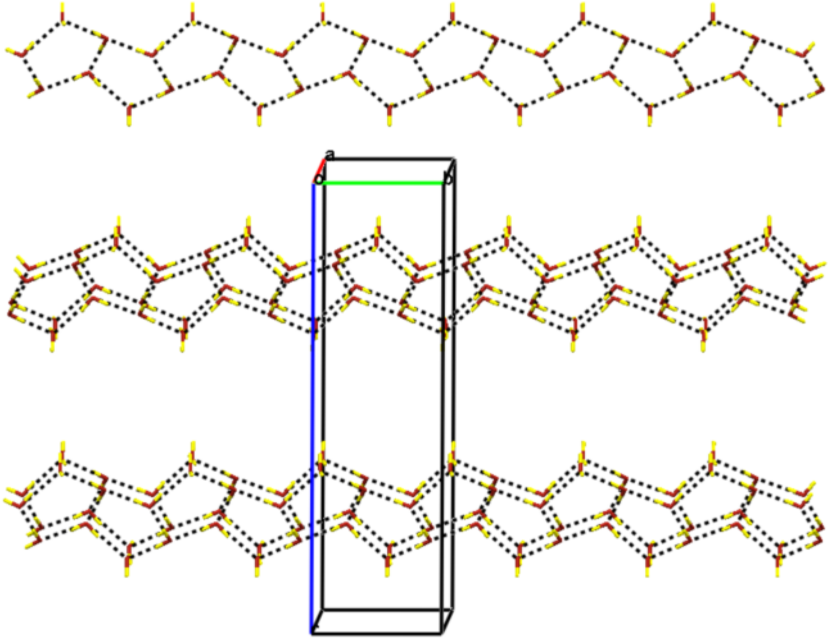


**Fig. 4** Cyclic pentamer water clusters formed by distinct intermolecular O−H···O and hydrogen bonds.

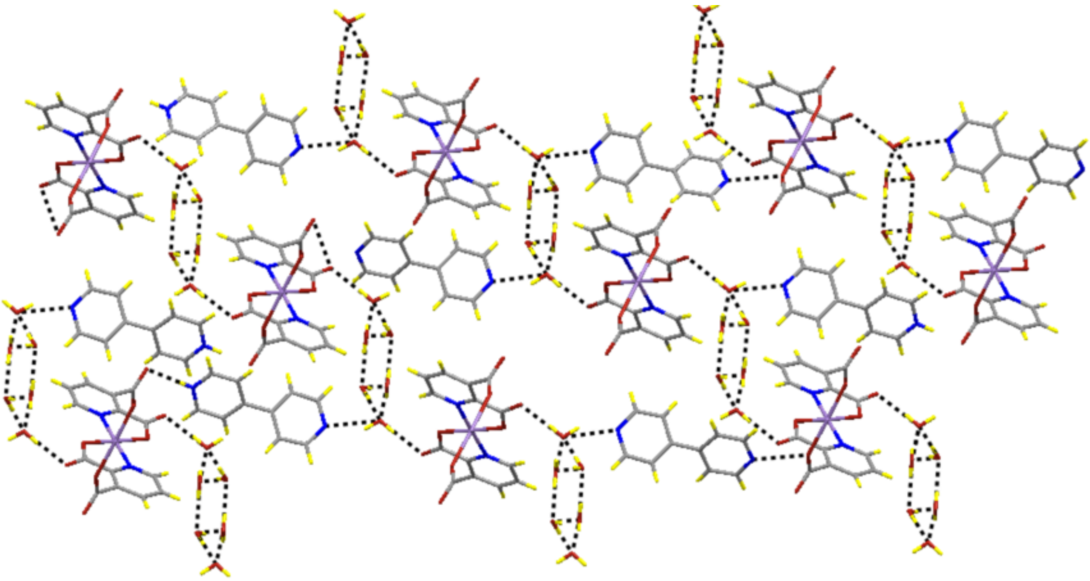


**Fig. 5** Hydrogen bonding between different species, the cyclic pentamer clusters brings together the cations and anions. Hydrogen bonds are shown as dashed lines.

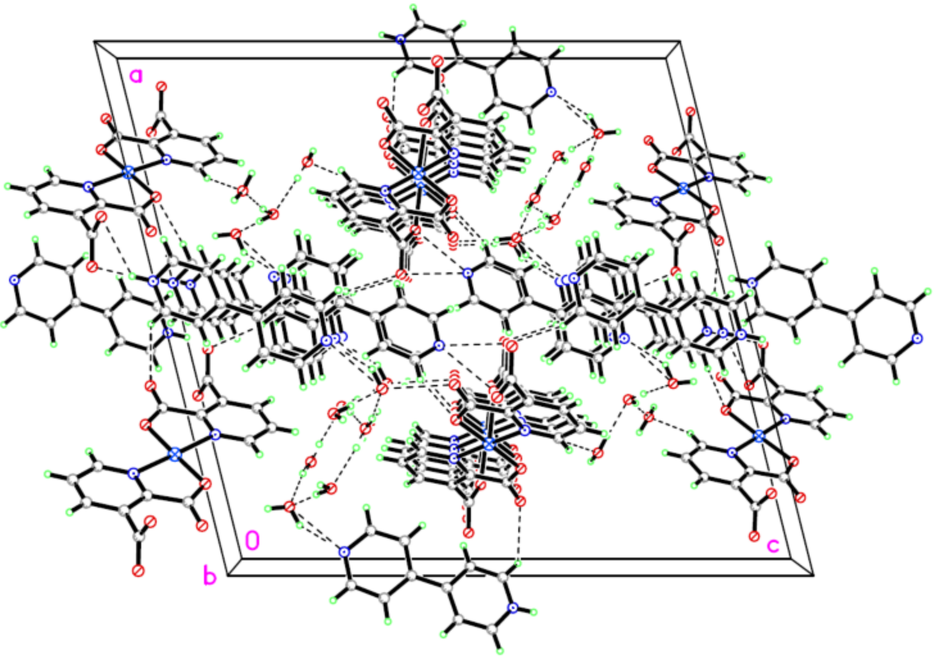


**Fig. 6** Crystal packing diagram of the title compound. Hydrogen bonds are shown by dashed lines.

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