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Influence of biphenyl spacer appended to the flexible phosphonate arms in modulating the dimensionality of the coordination polymers: Synthesis, structural chemistry and magnetic properties

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ABSTRACT

Two new compounds $[Co\,(2,2'\text{-bipy})\,(H_2dbp)]_n$ (**1**) and $[Ni\,(2,2'\text{-bipy})_2(H_2dbp)(H_2O)]\cdot H_2O$ (**2**) based on the flexible ligand 4,4′-dimethylenebiphenyldiphosphonic acid (H_4dbp) with 2,2′-bipyridine as secondary ligand have been synthesized under hydrothermal conditions. Both the compounds are well characterized by routine elemental analysis, IR, electronic spectroscopies, thermogravimetric analysis and finally by single crystal X-ray diffraction analysis. Compound **1** is a 1D extended coordination polymer and **2** is a discrete molecular compound. A comparative study between the geometries of H_4dbp ligand (in compounds **1** and **2**, present study) and p-xylylenediphosphonic acid (H_4pxp) ligand (in previously reported compounds $[Cu(2,2'\text{-bipy})(H_2pxp)]\cdot nH_2O$ (**1A**) and $Ni(2,2'\text{-bipy})_2H_4pxp]_n[H_2pxp]_n$ (**2A**), see text) demonstrate the effect of the twisting in the benzene rings in changing higher dimensional H_xpxp (x refers to number of protonated hydroxyl groups) compounds to lower dimensional H_xdbp compounds. The eight membered Co-dimer rings formed in compound **1** represents the simple and isolated Co-dimer, exhibiting weak antiferromagnetic exchange between metal centers through OPO bridges.

1. Introduction

Metal organic frameworks or coordination polymers are the class of materials that subject to enormous interest in the recent years in prospects of potential applications, such as, storage materials for gases, hi-capacity adsorbents, catalysis, bio-medical imaging [1]. Carboxylates constitute the major part of these functional materials to show high surface areas and uniform pore size distributions [2]. On the other hand, metal organophosphonates are among the earliest and most extensively studied examples of extended coordination architectures [3]. Clearfield et al. reported several metal phosphonates and explored the structural chemistry relevant to functional applications [4]. In contrast to carboxylates, phosphonates have strong tendency to coordinate with the metal centers, but the major problem in preparing crystalline phosphonate based MOFs is the less solubility of these materials [5]. The solubility of the metal phosphonates decreases as the valency of the metal atom increases. Usually phosphonates are having a propensity to form dense packed layered structures with general formula $M_x[O_3P(\text{organic spacer})PO_3]_y$ which are not porous in nature [6]. The topology of the layered structures can be modified to porous structures by introducing secondary ligands, such as, 2,2′-bipyridine, 1,10-phenanthroline etc. It is worth mentioning that, the introduction of secondary ligands leads to formation of not only extended coordination structures with well defined channels but also increases the solubility which often hinders in formation of crystalline materials [7].

Different types of organic spacers, such as, aromatic [8], alkyl [9], heterocyclic [10], etc. are used in obtaining metal phosphonates. Rigid aromatic spacers, such as, 1,4-benzenebisphosphonic acid and 4,4′-biphenyl bisphosphonic acid are used widely to obtain several compounds that feature layered structures. Some of the metal phosphonates, obtained by using these phosphonic acids, have less solubility and are characterized by powder X-ray diffraction instead of single crystal methods [11]. The attachment of flexible groups *i.e.* CH_2 groups to these rigid ligands results in the flexible ligands that can also form a layered structure as shown by rigid ligands. But introduction of secondary ligands along with flexible ligands offers us to study the different conformations of the ligands which enable us to design the desirable frameworks and also increases the solubility of the compounds formed. P-xylylenediphosphonic acid (H_4pxp) is a well defined flexible ditopic ligand which was studied elaborately with and without secondary ligands [12]. Recently, we have reported both *cis* and *trans* conformations of H_4pxp ligand in the same compound $[Ni(2,2'\text{-bipy})_2\textit{cis}\text{-}H_4pxp]_n[\textit{trans}\text{-}H_2pxp]_n$ by blocking the coordination sites of the Ni(II) polyhedra with the

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secondary ligand 2,2′-bipy [13]. Later on, Sun et al., also reported similar type of 1D compound, with Cd(II) ion and 2,2′-bipy as secondary ligand, and 3D compound with 1,10-phen as secondary ligand [14]. Very recently, we have described about the factors affecting the conformational modulation of flexible ligands in the self assembly process of coordination polymers of carboxylic acids [15]. By introducing the flexible CH_2 groups to the 4,4′-biphenyl bisphosphonic acid, it results in the formation of versatile ligand 4,4′-dimethylenebiphenyldiphosphonic acid (H_4dbp). The versatility of this ligand is the twisting of the phenyl rings in the biphenyl spacer changes the orientation of the flexible CH_2 groups that has impact on the coordination modes of the PO_3H_2 groups [16]. Here, we report two compounds [Co (2,2′-bipy) (H_2dbp)]$_n$ (**1**) and [Ni (2,2′-bipy)$_2$(H_2dbp) (H_2O)] $\cdot$ H_2O (**2**), based on phosphonic acid H_4dbp and secondary ligand 2,2′-bipyridine with Co and Ni metals which are known to exist in square pyramidal and octahedral geometries respectively. The influence of the phenyl ring twisting in the biphenyl spacer of H_4dbp ligand (compounds **1** and **2**, present study) is discussed in detail in comparison with the H_4pxp ligand (compounds Cu(2,2′-bipy)(H_2L)]$_n$ $\cdot$ $n$$H_2O$ (**1A**) and [Ni(2,2′-bipy)$_2$$H_4$pxp]$_n$ [H_2pxp]$_n$ (**2A**), previously reported). Variable temperature magnetic susceptibility measurements of the compound **1** have been performed and the results are fitted through the theoretical equations to obtain the magnitude of the exchange parameter.

2. Experimental

2.1. Materials and physical measurements

All the chemicals were received as reagent grade and used without any further purification. H_4dbp was prepared according to the reported procedure [17]. Elemental analyses were determined by FLASH EA series 1112 CHNS analyzer. Infra red spectra of solid samples obtained as KBr pellets on a JASCO-5300 FT-IR spectrophotometer. Thermogravimetric analyses were carried out on a STA 409 PC analyzer and corresponding masses were analyzed by QMS 403 C mass analyzer, under the flow of N_2 gas with a heating rate of 5 °C min^{-1}, in the temperature range of 30–1000 °C. The electronic absorption spectra have been recorded on a Cary 100 Bio UV–visible spectrophotometer at room temperature. Magnetic susceptibilities were measured in the temperature range 2–300 K on a Quantum Design VSM-SQUID. The compounds were synthesized in 23 mL Teflon-lined stainless vessels (Thermocon, India).

2.2. Synthesis of compound (**1**)

A mixture of $CoSO_4 \cdot 7H_2O$ (0.097 g, 0.348 mmol), 2,2′-bipyridine (0.05 g, 0.320 mmol), H_4dbp (0.149 g, 0.436 mmol), H_2O (10.0 g, 555 mmol) in mole ratio 1.08:1:1.3:1735 were stirred under air atmosphere for few hours. The solution was transferred into Teflon-lined stainless steel vessel (23 mL), sealed and heated up to 180 °C for 72 h. By slow cooling of the reaction mixture to room temperature over 48 h red block crystals were obtained. Yield: 62% (based on Co) $C_{24}H_{22}CoN_2O_6P_2$ (555.31): calcd. C 51.91, H 3.99, N 5.04; found C 52.09, H 4.19, N 5.58. IR (KBr pellet) (υ/cm^{-1}): 2905, 1597, 1496, 1473, 1439, 1408, 1205, 1130, 1080, 1020, 922, 835, 765, 734, 592, 526, 474.

2.3. Synthesis of compound (**2**)

The same synthetic procedure was used to synthesize **2** as that for **1** except $NiSO_4 \cdot 7H_2O$ was used instead of $CoSO_4 \cdot 7H_2O$. Yield: 38.4% (based on Ni). $C_{34}H_{34}N_4NiO_8P_2$ (747.30): calcd. C 54.65, H 4.58, N 7.49; found C 55.39, H 4.09, N 7.99. IR (KBr pellet) (υ/cm^{-1}): 3477, 3354, 3059, 1658, 1599, 1568, 1494, 1440, 1317, 1248, 1161, 1068, 1022, 885, 765, 734, 590, 536, 470.

Table 1
Crystallographic data of the compounds **1** and **2**.

	1	**2**
Formula	$C_{24}H_{22}CoN_2O_6P_2$	$C_{34}H_{34}N_4NiO_8P_2$
FW	555.31	747.30
T(K)/ λ(Å)	298/0.71073	298/0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a/Å	10.959(2)	10.670(2)
b/Å	11.028(2)	11.900(2)
c/Å	11.353(2)	14.080(3)
α [deg.]	75.62(3)	77.80(3)
β [deg.]	83.96(3)	68.46(3)
γ [deg.]	62.63(3)	82.23(3)
Volume (Å^3)	1180.2(4)	1622.1(5)
Z, ρ_{cal}/Mg m^{-3}	2, 1.563	2, 1.530
μ (mm^{-1}), F(000)	0.907,570	0.757,776
Goodness-of-fit on F^2	1.035	1.059
$R1/wR2$ [$I > 2\sigma(I)$]	0.0505/0.1067	0.1087/0.1503
$R1/wR2$ (all data)	0.0813/0.1209	0.1981/0.1936
Largest diff. peak and hole [e Å^{-3}]	0.629 and −0.369	1.006 and −0.476

2.4. X-ray crystallography

Crystal data of the compounds was collected on Oxford Gemini Diffractometer equipped with EOS CCD detector at 298 K. Monochromatic Mo$K\alpha$ radiation (0.71073 Å) was used for the measurements. The data were reduced by using SAINTPLUS [18] and a multi-scan absorption correction using SADABS [18] was performed. Structure solution and refinement were done using programs of SHELX-97 [19]. All the non hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the carbon atoms were introduced on calculated positions and included in the refinement riding on their respective parent atoms. Attempts to locate the hydrogen atoms for the solvent water molecule in compound **2** through Fourier electron density were failed. However, no attempts were made to fix these atoms on their parents. The hydrogen atoms on the P–OH groups in the compounds are fixed by the proper HFIX commands. Due to tiny crystals of compound **2**, we obtain slightly poor quality data which reflects in R factor and R_{int} values slightly greater than the expected limits. Table 1 summarizes the structural data and refinement parameters of the studied crystals. The selected bond lengths, bond angles and hydrogen bonding parameters are presented in Table 2 and Table 3 respectively.

3. Results and discussion

Compounds **1** and **2** have been synthesized by a direct one pot reaction of $M$$SO_4 \cdot 7H_2O$ (M=Co^{2+} and Ni^{2+}) with H_4dbp and 2,2′-bipyridine under hydrothermal conditions. Compounds **1** and **2** have been obtained as well-formed blocks. Both compounds are non-hygroscopic and stable in air and insoluble in common organic solvents and in water. The ratio of the reactants is optimized by doing several experiments to obtain compounds with moderate yield.

3.1. Structural description of [Co (2,2′-bipy) (H_2dbp)]$_n$ (**1**)

Compound **1** crystallizes in triclinic space group P-1. As shown in Fig. 1, Co(II) ion is present in square pyramidal CoN_2O_3

Table 2
Selected bond lengths (Å) and bond angles (deg.) of compounds **1** and **2**.

Distances	Bond lengths (Å)	Angles	Bond angles (deg.)
[Co (2,2′-bipy) (H_2dbp)]$_n$ (1)			
Co(1)–O(5)[a]	1.968(3)	O(5)[a]–Co(1)–O(4)[b]	118.46(12)
Co(1)–O(4)[b]	1.997(2)	O(5)[a]–Co(1)–O(1)	94.79(12)
Co(1)–O(1)	2.041(2)	O(4)[b]–Co(1)–O(1)	98.61(10)
Co(1)–N(1)	2.111(3)	O(5)[a]–Co(1)–N(1)	109.75(11)
Co(1)–N(2)	2.160(3)	O(4)[b]–Co(1)–N(1)	127.04(11)
P(1)–O(1)	1.497(2)	O(1)–Co(1)–N(1)	97.92(11)
P(1)–O(2)	1.515(2)	O(5)[a]–Co(1)–N(2)	84.70(12)
P(1)–O(3)	1.562(3)	O(4)[b]–Co(1)–N(2)	87.50(11)
P(2)–O(5)	1.469(3)	O(1)–Co(1)–N(2)	173.27(10)
P(2)–O(4)	1.498(2)	N(1)–Co(1)–N(2)	76.01(11)
P(2)–O(6)	1.567(3)		
[Ni (2,2′-bipy)$_2$(H_2dbp)(H_2O)]· H_2O (2)			
Ni(2)–N(2)	2.069(7)	N(2)–Ni(2)–N(3)	169.4(3)
Ni(2)–N(3)	2.072(7)	N(2)–Ni(2)–O(2)	94.4(3)
Ni(2)–O(2)	2.076(6)	N(3)–Ni(2)–O(2)	92.2(3)
Ni(2)–O(7)	2.077(6)	N(2)–Ni(2)–O(7)	96.4(3)
Ni(2)–N(4)	2.080(8)	N(3)–Ni(2)–O(7)	91.8(2)
Ni(2)–N(1)	2.082(7)	O(2)–Ni(2)–O(7)	90.6(2)
P(1)–O(2)	1.509(6)	N(2)–Ni(2)–N(4)	95.7(3)
P(1)–O(3)	1.510(6)	N(3)–Ni(2)–N(4)	78.5(3)
P(1)–O(1)	1.567(5)	O(2)–Ni(2)–N(4)	168.8(2)
P(1)–C(21)	1.788(10)	O(7)–Ni(2)–N(4)	83.5(3)
P(2)–O(6)	1.480(6)	N(2)–Ni(2)–N(1)	78.7(3)
P(2)–O(4)	1.517(6)	N(3)–Ni(2)–N(1)	92.9(3)
P(2)–O(5)	1.586(5)	O(2)–Ni(2)–N(1)	91.2(3)
		O(7)–Ni(2)–N(1)	174.9(3)
		N(4)–Ni(2)–N(1)	95.5(3)

Symmetry transformations used to generate equivalent atoms:
[a] $-x+1, -y+1, -z+1$
[b] $x-1, y+1, z-1$

Table 3
Hydrogen bonding table for compounds **1** and **2**.

D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A (deg.)
[Co (2,2′-bipy) (H_2dbp)]$_n$ (1)				
O(6)–H(6A)…O(2)[a]	0.89(5)	1.77(5)	2.638(4)	165(5)
O(3)–H(3A)…O(2)[b]	0.77(5)	1.87(5)	2.643(4)	174(6)
[Ni (2,2′-bipy)$_2$(H_2dbp)(H_2O)]· H_2O (2)				
O(5)–H(5A)…O(3)[c]	0.82	1.82	2.639(8)	175.8
O(1)–H(1A)…O(4)[d]	0.82	1.82	2.609(8)	159.8
O(7)–H(70)…O(6)[e]	0.94(8)	1.81(8)	2.747(8)	170(7)

Symmetry transformations used to generate equivalent atoms:
[a] $x+1, y-1, z+1$
[b] $-x, -y+1, -z$
[c] $x, y, z-1$
[d] $x, y, z+1$
[e] $-x, -y+1, -z$

geometry constituted by the two nitrogen atoms from 2,2′-bipy ring and three oxygen atoms from three H_2dbp^{2-} ligands. The ligand H_2dbp^{2-} coordinates to the two Co(II) centers on either sides with different coordination modes (Supporting information Fig. 1). The PO_3H group on the arm C24–P2 of two H_2dbp^{2-} ligands bridges the two Co(II) ions in a typical μ_2 bridging mode to form an eight membered Co–$(OPO)_2$–Co ring leaving P–OH groups into the interstitial positions as shown in Fig. 2. The PO_3H group on the other arm C11–P1 of the same two H_2dbp^{2-} ligands connects the Co atoms of two eight membered rings through P=O group in μ_1 coordination mode at the apical positions leaving P–OH and P–O$^-$ into the interstitial positions. The P–O bonds are assigned based on the bond lengths that are in good agreement with the literature [20]. Two such types of H_2dbp^{2-} ligands with μ_1 and μ_2 coordination modes link the four Co atoms to form a closed loop as shown in Fig. 2. These loops are extended by other set of loops to form a 1D extended double chain as shown in Fig. 3. The ligand H_2dbp^{2-} anion exists in a typical *trans* conformation with antiperiplanar torsion angle of 177.7° between two phosphonic acid groups (viewed through P1–C11–C24–P2) and creates a separation of 14.91 Å between two metal centers. In the biphenyl skeleton of H_2dbp^{2-} ligand, the phenyl group connected to μ_1-PO_3H group twists from the phenyl group connected to μ_2-PO_3H by an angle of 16.46° (Scheme 2).

Usually in the flexible ligands, if the ligand exists in *trans* conformation it leads to formation of higher dimensional structures but in compound **1** the *trans* conformation of the H_2dbp^{2-} ligand forms a 1D chain with $Co_2(H_2dbp)_2$ loops as shown by generally *cis* conformation. This is probably due to availability of more number of oxygen atoms on the phosphonate groups (PO_3H) and also the minor twist in the benzene rings of the biphenyl spacer that tends to form a closed loops rather than extended structures. As anticipated, the classical hydrogen bonding is observed between the P–OH groups of two adjacent 1D chains. The P–OH groups present on the arm in which PO_3H group exhibits μ_1 coordination mode are involved in the strong hydrogen bonding between two adjacent 1D chains to from a 2D supramolecular sheet (Fig. 4).

3.2. [Ni (2,2′-bipy)$_2$(H_2dbp)(H_2O)]·H_2O (2)

Compound **2** is a discrete compound that crystallizes in triclinic space group *P*-1. The relevant crystal structure consists of dipositive Ni ion in distorted NiN_4O_2 octahedral environment constituted by two bipyridine ligands; H_2dbp^{2-} ligand, one coordinated aqua ligand and one lattice aqua ligand (Fig. 5). Two bipyridine ligands block the three equatorial coordination sites and one apical coordination site of the Ni(II) octahedron leaving one equatorial and one apical sites for coordination with the phosphonic acid. The Ni–N bond distances are in the range of 2.071–2.082 Å. The residual equatorial site is coordinated by the

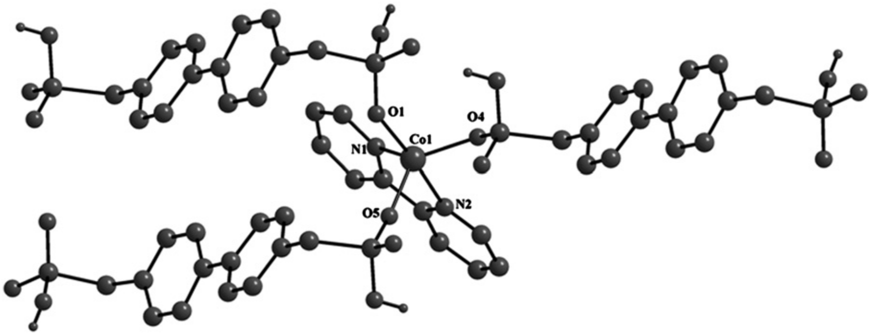


Fig. 1. Molecular diagram of compound **1** with metal polyhedra labeling.

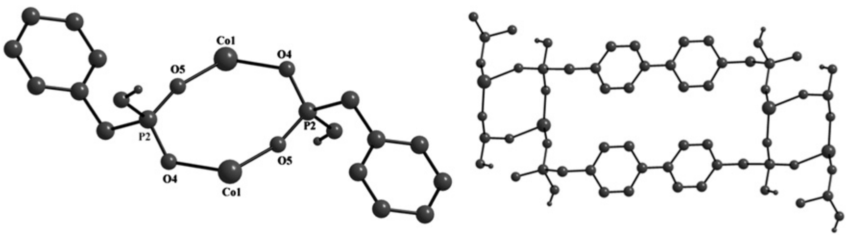


Fig. 2. Eight membered Co-dimer ring formed in compound **1** (left), pair of Co-dimers connected by the pair of H_2dbp^{2-} ligands to form a closed loop (Right).

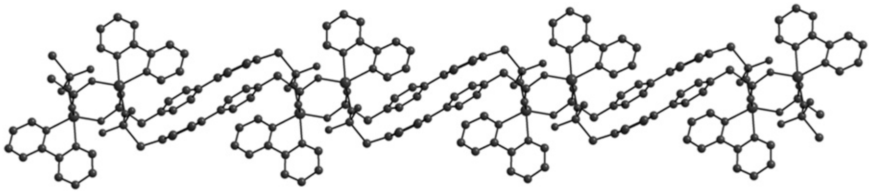


Fig. 3. 1D extended double chain formed in the crystal structure of compound **1**.

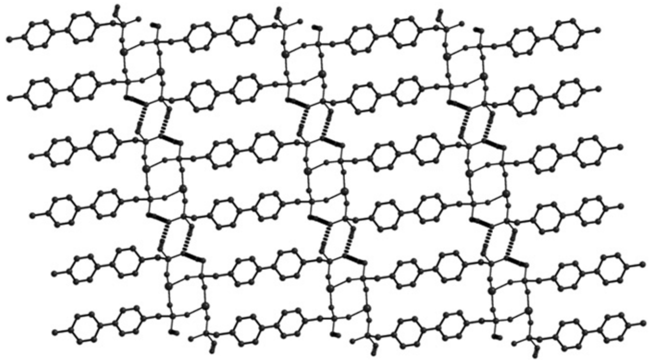


Fig. 4. 2D supramolecular network formed due to hydrogen bonding between the P–OH groups of the adjacent chains.

phosphonic acid H_4dbp in the dianionic form H_4dbp^{2-} through the P=O group and the remaining apical site is coordinated by the aqua ligand with Ni–O distance of 2.077 Å. One arm of the H_2dbp^{2-} ligand is coordinated to the metal polyhedra through P=O group, with μ_1 coordination mode leaving P–OH and P–O$^-$ groups into interstitial positions and the other arm (PO_3H) remains uncoordinated resulting in a discrete molecular structure rather than coordination polymer.

In the biphenyl skeleton of H_2dbp^{2-} ligand, the phenyl ring connected to the non-coordinated PO_3H arm is twisted from the phenyl ring connected to the coordinated PO_3H arm by a large angle of 39.04° (Scheme 2); consequently the orientation of CH_2–PO_3H group of the twisted phenyl ring completely deviates from the mean position (Supporting information Fig. 2). Further the two CH_2–PO_3H groups of H_2dbp^{2-} ligand are twisted with respect to each other by an antiperiplanar torsion angle of 157.51°. The formation of discrete structure apart from the extended coordination structure is mainly attributed to the large twisting of the phenyl ring in the biphenyl skeleton from the mean position.

Due to presence of P–OH groups, classical hydrogen bonding was observed between the molecular structures. The P–OH group on the non-coordinated PO_3H arm of one molecular compound is strongly connected to the P–O$^-$ group of the coordinated PO_3H arm of other molecular compound and vice versa through hydrogen bonding to form an eight membered $R_2^2(8)$ ring (Table 3). This type of connectivity leads to form a 1D supramolecular chain along the crystallographic *b* axis as shown in Fig. 6.

3.3. Effect of length of the bisphosphonic acid

In our previous report, we described two isomorphous structures of general formula $[M(2,2'\text{-bipy})_2H_4pxp]_n[H_2pxp]_n$ (M=Co(II) and Ni(II)) with p-xylylenediphosphonic acid and 2,2′-bipy as secondary ligand [13]. 2,2′-bipy blocks the four coordination sites at the metal polyhedra and allows only two sites for the H_xpxp (x refers to protonated hydroxyl groups) to coordinate with the metal center. In order to meet this coordination requirement (*i.e.* to satisfy the coordination sites: one equatorial and one apical sites) a flexible non-rigid ligand H_xpxp has adopted a rare *cis* conformation in neutral form and thereby the charge is neutralized by the *trans* conformation of H_xpxp in anionic form. These two compounds are classical examples that feature the flexibility of the ligand to exist in both *cis* and *trans* conformations to meet the coordination geometry at the metal center. In the present study, we extend the length of the phosphonic acid by increasing one phenyl ring (H_4dbp) to investigate the effect on the final structures (See Scheme 1). Thus by introducing the other phenyl ring into the spacer, the twisting of two phenyl rings with respect to each other in the biphenyl moiety plays an important role in the self assembly process. The coordination environment of the metals is different in both the compounds *i.e.*, square pyramidal in compound **1** and octahedral in compound **2**.

In compound **1**, Co(II) ion is present in square pyramidal geometry in which two sites are blocked by the 2,2′-bipy ring and the remaining three coordination sites are occupied by the oxygen atoms from the three H_2dbp^{2-} ligands. Compound **1** is stoichiometrically related to our previously reported compound $Cu(2,2'\text{-bipy})(H_2L)]_n \cdot nH_2O$ (**1A**) in which the spacer in the phosphonic acid is mono phenyl ring [21]. The coordination environment and the protonation state of the phosphonic acids is same in both the compounds but **1** is 1D double chain whereas **1A** is a 2D layer. The difference in the dimensionality of these two compounds is mainly due to increase in the length of the spacer in the phosphonic acid by one phenyl ring (present study) which creates a twisting in the biphenyl group thereby the flexible arm adopt different orientations. As shown in Fig. 7, in compound **1A**, two types of phosphonic acids are present in the crystal structure which differs in terms of coordination mode. The bridging H_2pxp bridges the Cu(II) atoms in μ_2 coordination mode to form a eight membered Cu-dimer rings and extended by the p-xylyl linkers to form a 1D chain and these chains are linked by the linking H_2pxp^{2-} ligand in μ_1 coordination mode to form a 2D network.

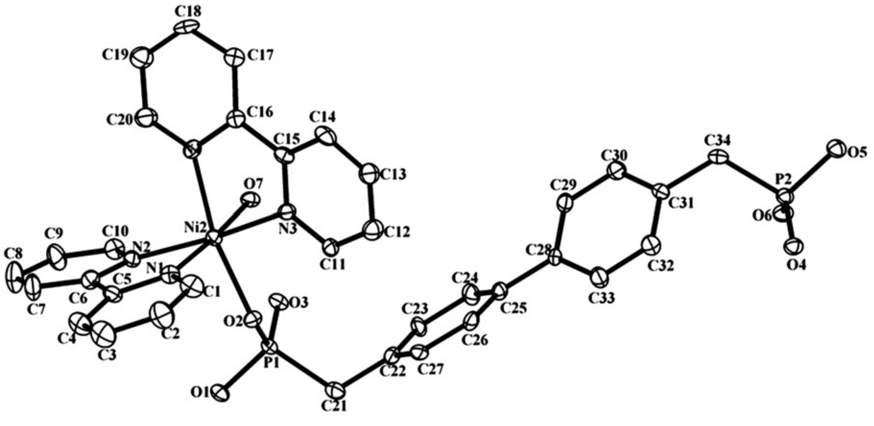


Fig. 5. ORTEP diagram of compound **2** at 30% probability level (hydrogen atoms are omitted for clarity).

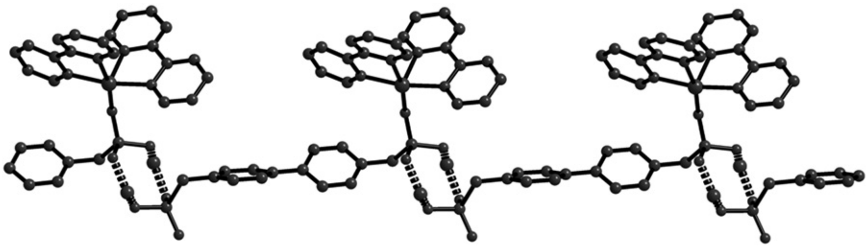
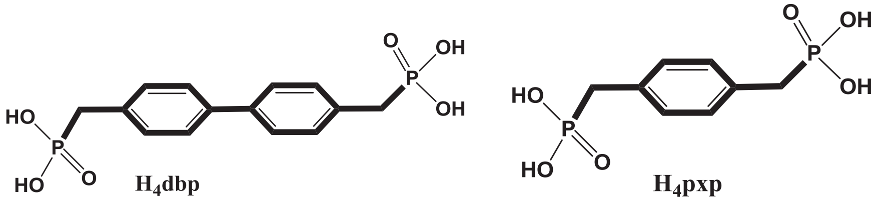
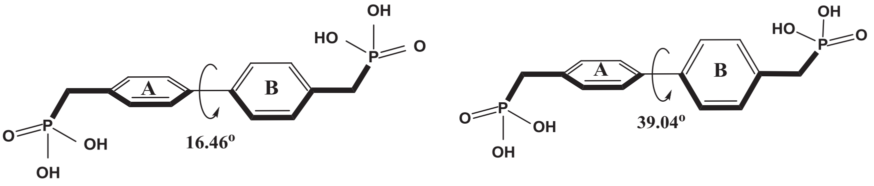


Fig. 6. 1D supramolecular chain formed due to hydrogen bonding between the adjacent molecular units.



Scheme 1. 4,4′-dimethylenebiphenyldiphosphonic acid (H_4dbp) and p-xylylenediphosphonic acid (H_4pxp).



Scheme 2. Scheme representing the twisting of the benzene rings in the biphenyl spacer of the H_2dbp^{2-} in compounds **1**(Left) and **2** (Right).

But interestingly in compound **1**, the PO_3H groups in the phosphonic acid H_2dbp^{2-} adopt different coordination modes on either arms (*i.e.*, μ_1 on one arm and μ_2 on another arm). As shown in Fig. 7, one arm of H_2dbp^{2-} adopts μ_2 coordination mode and expected to adopt same coordination mode on other side. However, due to twisting of the phenyl ring B from the phenyl ring A by an angle of 16.46° (See Scheme 2) it changes the orientation of the PO_3H groups on the phenyl ring B that tends to adopt μ_1 coordination mode rather than μ_2 to meet the coordination geometry of the metal ion. This minor twist of the phenyl ring in the biphenyl skeleton changes the orientation of the CH_2–PO_3H groups on the phenyl ring B to adopt a different coordination mode as a result 1D double chains are formed in the compound **1** (Fig. 7). Wang et al., also reported a 1D compound $[Cu_2(phen)_2(H_3dbp)_2(H_2dbp)]_n$ based on biphenyl bisphosphonic acid in which two types of $H_x$dbp ligands are present in the crystal structure which differs mainly in the protonation states and adopts same coordination mode [22]. The two Cu(II) ions are linked by a pair of H_3dbp^{1-} ligands to form a molecular boxes and these boxes are linked by the H_2dbp^{2-} ligand to form a 1D extended chains.

Compound **2** elaborately explains the effect of the twisting of the phenyl ring in the biphenyl skeleton in forming the low dimensional structures. The situation in compound **2** can be explained by comparing with our previously reported compound $[Ni(2,2'\text{-bipy})_2H_4pxp]_n[H_2pxp]_n$ (**2A**) [13]. In both the compounds, the Ni ion is present in octahedral environment, in which three equatorial and one apical coordination sites are blocked by the two 2,2′-bipy rings to form $[Ni(\square)_{eq}(\square)_{ap}(2,2'\text{-bipy})_2]^{2+}$ ($\square$ = vacant site) cation. In compound **2A**, H_4pxp adopts the rare *cis* conformation to meet the coordination geometry created by the 2,2′-bipy rings at the metal center (i.e. one equatorial and one

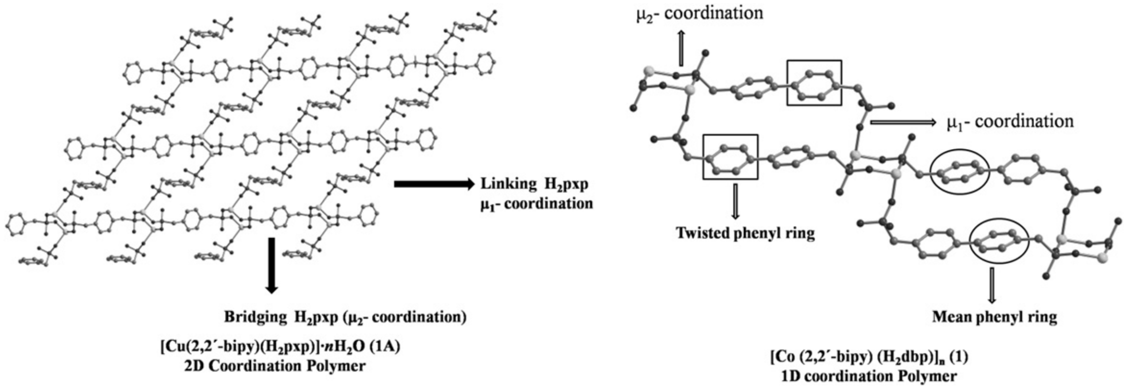


Fig. 7. 2D packing diagram of Compound **1A** showing the coordination modes of the H_2pxp^{2-} ligand (left); 1D chain of compound **1** viewing the conformation and coordination modes of the H_2dbp^{2-} ligand (Right).

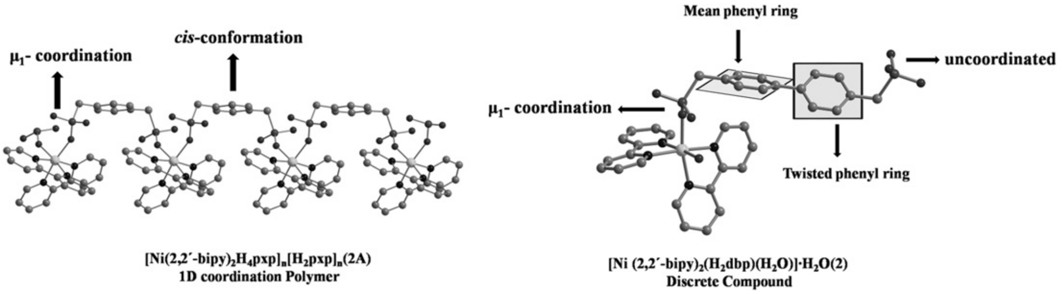


Fig. 8. 1D cationic chain formed in the compound **2A** viewing the conformation and coordination of the H_2pxp^{2-} ligand (left); Discrete compound **2** showing the mean and twisted phenyl rings in the H_2dbp^{2-} ligand (Right).

apical) resulting in a 1D chain [Ni(2,2′-bipy)$_2$ *cis*-H_4pxp]$_n^{2+}$ and the charge is neutralized by the ligand H_2pxp^{2-} as lattice component in *trans* from. In the complex cation [M(□)$_{eq}$(□)$_{ap}$(2,2′-bipy)$_2$]$^{2+}$ the linker phosphonic acid has only possibility to exist in the *cis* conformation to link the two cations. Recently Sun et al., also reported a compound similar to **2A** with cadmium [14] which supports that only *cis* conformation of the flexible phosphonic acid has tendency to link this type of complex cations to form an extended 1D chains. In a similar way in compound **2** (present work), the phosphonic acid H_4dbp in its neutral from or anionic form (H_2dbp^{2-}) has to adopt *cis* conformation to meet the coordination vacancies in the complex cation [Ni(□)$_{eq}$(□)$_{ap}$(2,2′-bipy)$_2$]$^{2+}$. In compound **2**, the residual equatorial site is coordinated by the H_2dbp^{2-} through P═O group and the other end should be coordinated to the apical site by adopting the *cis* conformation. But due to biphenyl spacer in the phosphonic acid the phenyl ring B twists from the mean plane by an large angle of 39.04° and changes the orientation of the PO_3H groups on the flexible arm as a result it does not meet the coordination geometry at the metal center and does not link the complex cations (Fig. 8). The twisting of the phenyl ring B to a large extent completely changes the direction of the PO_3H groups, as a result, it does not meet the required conformation (*i.e.*, *cis*) to act as a linker; consequently the molecular complex does not extend to the 1D polymer and remains as a discrete compound. The resulting complex [Ni(2,2′-bipy)$_2$(H_2dbp)] accommodates the water molecule into the apical site to furnish the octahedral geometry.

Based on the aforementioned discussion, the attachment of rigid biphenyl spacer to the flexible phosphonate groups have an accountable role in directing the dimensionality of the final products. The combination of both the twisting in benzene rings and the flexible nature of the CH_2 groups changes the orientation of the phosphonate groups. Due to this multiple effect, the two fold axis of symmetry in H_2dbp^{2-} is absent in both the compounds and the CH_2–PO_3H groups are twisted with respect to each other by a torsion angle of 177.79° and 157.49° in the compounds **1** and **2** respectively instead of 180.0°. The similar type of spacers (CH_2–C_6H_4–C_6H_4–CH_2) were also reported with imidazoles (4,4′-bis(imidazol-1-ylmethyl)biphenyl) [23] and triazoles (4,4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl) [24]. But this effect does not show any influence in the dimensionality of the final compounds, because these ligands are only monodentate with μ_1 coordination mode. Metal carboxylates based on this ligand are not reported in the literature. As the number of coordinating atoms in the coordinating group increases, the coordination modes also increases, as result even a small twist in the phenyl rings of biphenyl spacer shows a major difference in the dimensionality as in the case of the phosphonates discussed here.

4. Electronic spectroscopy

Both the compounds are additionally characterized by the solid state electronic absorption spectroscopy. The relevant electronic spectra of both compounds compared with the phosphonic acid H_4dbp is shown in Fig. 9. Both the compounds show similar absorption peaks as displayed by the H_4dbp ligand. But there is a well defined *d*–*d* transition in the compound **1** in the region 450–555 nm which contains Co(II) ion.

5. Thermal properties

TGA curves are made under flowing N_2 for the compounds **1** and **2** in the temperature range 30–1000 °C (Fig. 10). Compound **1** shows thermal stability up to 320 °C with weight loss of 6.2% attributed to condensation of hydroxyl groups of the phosphonate ligands (theoretical values of 6.48%). From 320 to 900 °C

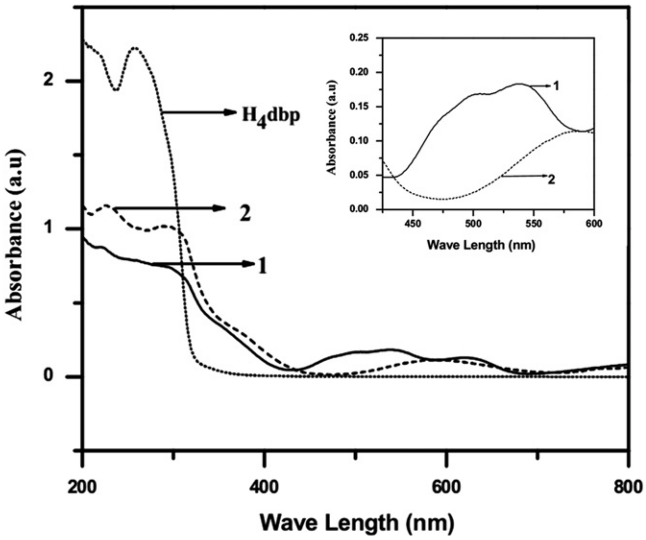


Fig. 9. Diffused reflectance electronic absorption spectra of compounds **1** and **2** in comparison with the H_4dbp (Inset graph shows the *d–d* transition in compound **1**).

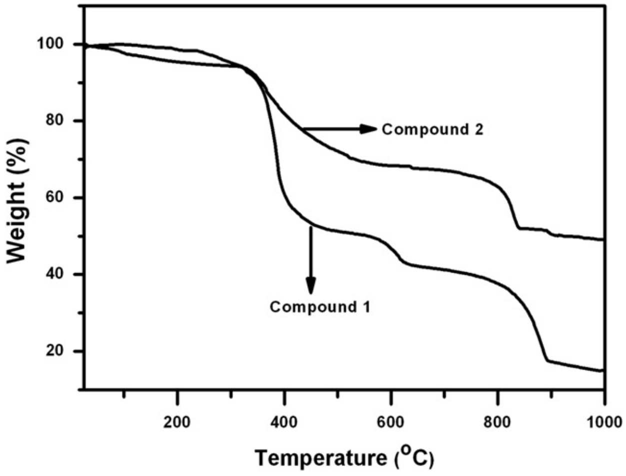


Fig. 10. Thermogravimetric curves for compounds **1** and **2.**

compound **1** undergoes continues weight losses in three steps due to combustion of organic groups 2,2′-bipyridine and biphenyl rings. The final end product is supposed to be $Co(PO_3)_2$ with a formula weight of 216.0 (38%) but the observed weight remained at 1000 °C is 83.25 (15%). The difference in the weight, observed, is due to initial loss of water molecules due to condensation and loss of P_2O_5 from the residual mass. The overall decomposition and stability of the compound **1** follows the normal pathway as described for the metal phosphonates. Compound **2** is discrete compound and shows stability up to 290 °C with weight loss of 4.2% attributed to one coordinated and one lattice molecule (theoretical values of 4.8%) and undergoes continues weight losses up to 850 °C due to combustion of organic groups and shows constant residual mass of 366.3 (49.2%) up to 1000 °C. The final end product is supposed to be $Ni(PO_3)_2$ with a formula weight of 216.0 (38%) but the increase in the residual mass at 1000 °C is due to retention of some P_2O_5.

6. Magnetic properties

A variable temperature magnetic susceptibility measurement of the compound **1** was performed in the temperature region of 2–300 K in an applied dc field of 1 K Oe. Both χ_M vs. T and $\chi_M T$ vs. T plots were shown in the Fig. 11. (where χ_M is the magnetic susceptibility). The room temperature (300 K) $\chi_M T$ product amounts to 5.48 $cm^3\,K\,mol^{-1}$, which is higher than the expected value of 3.75 $cm^3\,K\,mol^{-1}$ for two isolated high-spin Co(II) ions ($g=2$ and $S=3/2$). As the temperature is lowered, the $\chi_M T$ value continuously decreases to 4.27 $cm^3\,K\,mol^{-1}$ at 22 K and then sharply decreases up to 2 K reaching a minimum value of 1.34 $cm^3\,K\,mol^{-1}$. The $1/\chi_M$ vs. T plot follows the Curie–Weiss law with negative Weiss constant $\Theta=-8.7$ K. The decrease in $\chi_M T$ value with temperature and negative Weiss constant suggest antiferromagnetic interactions between the two Co(II) centers. The magnetic data were fitted assuming the phosphonate bridges of the two Co(II) ions form a isolated spin dimer. By introducing inter-dimer magnetic coupling constant zJ' the magnetic susceptibility data from 2–300 K was fitted from the following equation which was deduced from the spin Hamiltonian [25].

$$H=-JS_1\cdot S$$

(where S_1 and S_2 are the spin operators with $S_1=S_2=3/2$)

$$E(S_T)=-JS_T(S_T+1)$$

$$S_T=0,\ 1,\ 2,\ 3.$$

$$E(S_T)=0,-J,-3J,-6J$$

$$\chi_M=\frac{\chi_M{}'}{\{1-\chi_M{}'(2zJ'/Ng^2\beta^2)\}}$$

$$\chi_M{}'=\left(\frac{2Ng^2\beta^2}{KT}\right)\left[\frac{A}{B}\right]$$

where

$$A=\left[\exp\left(\frac{J}{KT}\right)+5\exp\left(\frac{3J}{KT}\right)+14\exp\left(\frac{6J}{KT}\right)\right]$$

and

$$B=\left[1+3\exp\left(\frac{J}{KT}\right)+5\exp\left(\frac{3J}{KT}\right)+7\exp\left(\frac{6J}{KT}\right)\right]$$

The parameters N, β and K have their normal meanings. The best fit of the theoretical equation to the experimental data leads to the $g=2.332(2)$ $J=-0.685(2)\,cm^{-1}$ and $zJ'=-0.038(4)$ with agreement factor of 8.4×10^{-8} (where $R=\Sigma[(\chi_M T)_{exp}-(\chi_M T)_{cal}]^2/\Sigma(\chi_M T)^2_{exp}$).

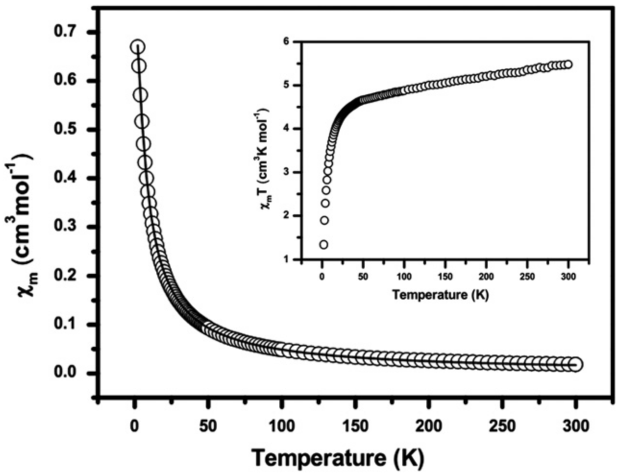


Fig. 11. χ_M vs. T in the temperature range of 2–300 K (Inset graph shows $\chi_M T$ vs. T) of compound **1**. The solid line indicates the fitting using theoretical model (see text).

The studies on magnetic behavior of isolated Co(II)-dimers bridged by the phosphonate bridges are very rare when compared to the carboxylate bridges. But the magnetic behavior of Co(II) ions bridged the phosphonate bridges to form an extended metal oxide coordination architectures are well studied. Clearfield et al., reported a compound $[Co_2(pxp)(H_2O)_2]$ in which the Co atoms are bridged by the phosphonate oxygen's to form a 2D metal oxide layers and the Co(II) ions shows a net antiferromagnetic interactions in these layers [12b]. But till date, an isolated Co-dimer bridged by the phosphonate bridges is not reported and compound **1** represents a classical example of such system. From the crystal structure of the compound **1**, the only possible path way for spin exchanges between two Co(II) ions is phosphonate bridges; no other pathways (either through hydrogen bonding or through short inter-dimer separation) are not possible. The magnitude of exchange parameter obtained through exchange between the Co(II) ions through the phosphonate bridges in the eight membered ring is very less indicating the weak σ pathway. The $\chi_M T$ value for compound **2** measured at room temperature is $1.06\ cm^3\ K\ mol^{-1}$, which is in good agreement with the theoretically predicted value for the single Ni(II) octahedral ion i.e. $1.0\ cm^3\ K\ mol^{-1}$ with $g=2$ and $S=1$. Due to absence of short contacts between the discrete metal complexes in the crystal structure of compound **2** (either through supramolecular or packing interactions), the exchange phenomenon between the Ni(II) ions would be negligible in compound **2**.

7. Conclusion

We have synthesized two compounds $[Co(2,2'\text{-bipy})(H_2dbp)]_n$ (**1**) and $[Ni(2,2'\text{-bipy})_2(H_2dbp)(H_2O)]\cdot H_2O$ (**2**) based on biphenyl spaced flexible ligand H_4dbp and secondary linker 2,2′-bipyridine. Compound **1** is a extended double chain, in which Co(II) ion is in square pyramidal geometry and compound **2** is a discrete compound, in which Ni(II) ion exists in octahedral geometry. The twisting of phenyl rings in the biphenyl spacer changes the orientation of the PO_3H groups of the H_2dbp^{2-} in compound **1** thereby the ligand adopt different coordination modes by the PO_3H groups on both ends resulting in the formation of 1D chains rather that 2D layers as obtained in case of H_4pxp ligand with same empirical formula. In a similar way, in compound **2**, the phenyl rings in the biphenyl spacer of the H_2dbp^{2-} ligand twist by a large angle of 39.04°. As a result the conformation of the H_2dbp^{2-} ligand changes and because of this, the ligand does not meet the coordination requirements at the metal center to link the metal polyhedra, thereby forming a discrete compound. The comparison of compounds **1** and **2** with the compounds based on the H_4pxp ligand reveals that twisting in the phenyl rings of the biphenyl spacer is accountable for obtaining low dimensional compounds. The effect is primarily pronounced in the multidentate ligands rather than monodentate ligands. Compound **1** represents a unique example, in which the simplest and isolated Co-dimer is bridged by the three-membered OPO bridges. Analysis of variable temperature magnetic susceptibility measurement curves of compound **1** show weak antiferromagnetic interactions between the metal ions through these OPO bridges.

Acknowledgments

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Appendix A. Supporting information

CCDC 880789 (for **1**), 880790 (for **2**), 878561 (for **1A**) and 748113 (for **2A**) contain the supplementary crystallographic data for compounds presented in the study. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Appendix B. Supplementary data

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2012.08.044.

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