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Same not the Same: Thermally-Driven Transformation of Nickel Phosphinate-Bipyridine 1D Chains into 3D Coordination Polymers

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ABSTRACT

Three 1D nickel coordination polymers (CPs) based on P,P'-diphenylethylenediphosphinic acid and three different bis-pyridine co-ligands, namely 4,4'-bipyridine (bipy), 1,2-bis(4-pyridyl)ethane (bpy-ane) and 1,2-bis(4-pyridyl)ethane (bpy-ene), were prepared in mild hydrothermal conditions from water solutions containing the dissolved reagents. The CPs have formula \([\text{Ni}(\text{H}_2\text{O})_4\text{(bipy)}\cdot \text{pc}_{2}\text{p}]_n \) (1),\([\text{Ni}(\text{H}_2\text{O})_4\text{(bpy-ane)}\cdot \text{pc}_{2}\text{p}]_n \) (2), and \([\text{Ni}(\text{H}_2\text{O})_4\text{(bpy-ene)}\cdot \text{pc}_{2}\text{p}]_n \) (3) and their structural features were investigated by single crystal X-ray diffraction, UV-VIS, FT-IR spectroscopies and magnetic measurements. They are constituted of infinite Ni(\text{H}_2\text{O})_4(bis-pyridine) 1D rows connected, through hydrogen bonds, with the phosphinic acids placed among adjacent rows. Although the formulas and the structural topologies of the three compounds are almost identical, they behave in different manners upon heating. Compound 1 yields an amorphous phase when water molecules are thermally removed, whereas compound 3 undergoes interesting phase transformations derived from the connection of Ni atoms with the phosphinates oxygen atoms, increasing the dimensionality to 3D and maintaining crystallinity. The behavior of compound 2 has some analogies to that of 3 although a complete structural characterization was not performed because of a significant crystallinity loss of the heated phase. The structural features were studied by means of combination of variable temperature (VT) single crystal and powder X-ray diffraction and thermogravimetric analysis. The reason for these different behaviors was ascribed to both the length and the flexibility degree of the nitrogenated co-ligands.
INTRODUCTION

Chemistry is about transformations. The large majority of chemical reactions are carried out in liquid media, being the molecules free of moving around and to assume conformations favorable to the reactions to take place. Metal-organic frameworks (MOFs), and coordination polymers (CPs) in general, are classes of compounds that can easily show structural transformations at the solid state driven by external stimuli, such as light, pressure and heat. The majority of the structural changes can be ascribed either to a modification of ligand conformation or to the removal of solvent molecules, usually placed in voids or in channels as crystallization solvent. Less frequently, the formation or breakage of some bonds are also events taking place upon external stimuli and they can occur through crystal-to-crystal or crystal-to-amorphous phase transformations. Understanding the factors that influence the structural transformations in these classes of solids is crucial to gain the ability to design new and more efficient materials. Crystal-to-crystal transformation induced by the loss of crystallization water or other solvents is a typical reaction already observed in several compounds. However, the majority of CPs or MOFs described in the literature exhibits reversible solvent loss and/or uptake, without changes in dimensionality: in other words, no strong bonds which increase the dimensionality are formed upon solvent loss. The reversibility of this event in flexible CPs, associated with structural transformation due to changes in ligand conformation, is typically called breathing effect. A large number of MOFs and CPs reported in literature shows this phenomenon. Systems with change of dimensionality of the system are rare to the best of our knowledge. On the contrary, CPs based on diphosphinate ligands (see chart 1) frequently show structural modifications induced by the temperature, leading also to changes of the dimensionality of the network. Diphosphinate linkers feature some chemical and geometrical similarities with carboxylate and phosphonate moieties (see chart 2). Diphosphinates have the advantage of being versatile in tuning the electronic and steric properties of the organic residues attached to the phosphorus atom.

Chart 1. Molecular structure of a diphenyl-bisphosphinate with different substituting groups.
Chart 2. Structural relationships among carboxylates, phosphonates and phosphinates.

As an example, the 3D network \([\text{Cu}(\text{pc}_2\text{p})(\text{bipy})(\text{H}_2\text{O})\cdot 2.5\text{H}_2\text{O}]_n\) (where \(\text{H}_2\text{pc}_2\text{p} = \text{P,P'}\text{-diphenylethlenediphosphinic acid}, \text{bipy} = 4,4'\text{-bipyridine}\)) converted in different crystalline phases when heated up to 120°C. Differently, in solution, it transformed into a 2D grid \([\text{Cu}(\text{pc}_2\text{p})(\text{bipy})(\text{H}_2\text{O})\cdot 3\text{H}_2\text{O}]_n\), showing a rare example of modification from 3D to 2D network. \(^{23}\) Moreover, by heating the iso-topological 2D grid \([\text{Cu}(\text{pxylp})(\text{bipy})(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}]_n\) (where \(\text{H}_2\text{pxylp} = \text{P,P'}\text{-diphenyl-p-xylylenediphosphinic acid}\)), the 3D network \([\text{Cu}(\text{pxylp})(\text{bipy})]_n\) was obtained. \(^{24}\) Finally, the metal-organic nanotubes (MONTs) having formula \([\text{Cu}(\text{pcp})(\text{bipy})(\text{H}_2\text{O})\cdot 2.5\text{H}_2\text{O}]_n\) [where \(\text{H}_2\text{pcp} = \text{P,P'}\text{-diphenylmethylenediphosphinic acid}, \text{bpy-ane} = 1,2\text{-bis(4-pyridyl)ethane}\)] displayed a very particular behavior: by heating the crystals up to 250°C, the water molecules were removed from the cavity but the framework remained unchanged. \(^{25,26}\) Above this temperature, the compounds started to decompose. On the contrary, when the crystal of MONT with bpy-ane was heated in water at 90°C for 30 days, the compound transformed into a 1D compound of formula \([\text{Cu}(\text{pcp})(\text{bpy-ane})(\text{H}_2\text{O})]_n\), a structural isomer without voids. In the same conditions, the analogous MONT with bipy remained unchanged. The reason of this behavior was attributed to the non-existence of a stable 1D phase for the latter due to a predicted thermodynamically unfavorable crystal packing. \(^{27}\) Herein, we report on the structural transformations observed in a novel class of nickel phosphinates containing bypiridine co-ligands. By adding together Ni and \(\text{pc}_2\text{p}\) with the three co-ligands showed in chart 3, namely bipy, bpy-ane and 1,2-bis(4-pyridyl)ethylene (bpy-ene), we obtained 1D coordination polymers of general formula \([\text{Ni}(\text{H}_2\text{O})_4(\text{bis-pyridine})\cdot \text{pc}_2\text{p}]_n\) and with similar crystal arrangement constituted by cationic 1D chains of \([\text{Ni}(\text{H}_2\text{O})_4(\text{bis-pyridine})]^2^+\). The polymers with bpy-ane and bpy-ene maintain an ordered crystal arrangement after heating and they undergo a crystal-to-crystal transformation into a 3D coordination network. The study of these transformations sheds some light on the mechanism of network formation in different but related systems, such as the M(II), pcp, bis-pyridines and the M(II), pc2p, bis-pyridines.
RESULTS AND DISCUSSION

Green crystals of \([\text{Ni(H}_2\text{O)}_4(bipy)\cdot\text{pc}_2\text{p}])_n\) (hereafter 1), \([\text{Ni(H}_2\text{O)}_4(bpy-ane)\cdot\text{pc}_2\text{p}])_n\) (hereafter 2) and \\
\([\text{Ni(H}_2\text{O)}_4(bpy-ene)\cdot\text{pc}_2\text{p}])_n\) (hereafter 3) were obtained by mixing in water nickel acetate, \(\text{H}_2\text{pc}_2\text{p}\) and \\
bipy (1) or bpy-ane (2) or bpy-ene (3) at 90°C. Crystal structures of the three compounds were \\
determined by single crystal X-ray diffraction analysis (Figure 1). All the structures are constituted of \\
cationic 1D chains of \([\text{Ni(H}_2\text{O)}_4(L)])^{2+}\) and dianionic diphosphinate moieties. This arrangement, formed \\
by a 1D string of metal, water and bis-pyridine intercalated by another anionic ligand, is relatively \\
common in literature and most of the reported structures were obtained as side products in the attempt to \\
synthesize 3D networks.28-50 The three compounds reported here are not isostructural and the space \\
groups are different, as reported in table 1. The calculated density for 1 (1.547 g/dm³) is larger than \\
those of 2 (1.421 g/dm³) and 3 (1.415 g/dm³).

Figure 1. Fragment of the structures of 1 (left), 2 (center) and 3 (right).
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<td>4</td>
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<td>0.0952</td>
<td>0.1008</td>
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In all cases, Ni(II) metal atom is octahedrally coordinated by four water molecules and by two nitrogen atoms belonging to two different bis-pyridine ligands. The Ni-O and Ni-N distances are comparable in the three compounds (see Table S1, ESI). The conformation of pc₂p can be defined using the C_{ipso}-P-P-C_{ipso} dihedral angle where C_{ipso} is the carbon atom of the phenyl ring bonded to the phosphorus atom.
The value of the angle is about 180° for all the structures. This value is one of the most recurrent in the pc2p complexes reported up to now.51 Strong hydrogen bonds, with O-O distances in the range 2.64-2.76 Å, exist between the water molecules and the oxygen atoms of the pc2p. The Ni(H2O)4 groups are surrounded by four pc2p anions and the oxygen atoms of the pc2p are connected with four different Ni(H2O)4 moieties. The H-bond network in 1 is different with respect to 2 and 3, as shown in Figure S1. Therefore, the whole supramolecular arrangement is different and it is schematically illustrated in Figure 2. The pc2p group is represented by a purple cylinder while the [Ni(H2O)4(bis-pyridine)]n column is schematized by a line formed by green cubes and light blue parallelepipeds. In 2 and 3, the cylinders and the cubes are arranged as in a chessboard, while in 1 the pc2p are intercalated between the lines of the [Ni(H2O)4(bis-pyridine)]n columns.

Figure 2. Schematic representation of the crystal packing for 1, 2 and 3. Purple cylinders represent pc2p groups; green cubes (Ni(H2O)4) and light blue parallelepipeds (bis-pyridine) are used to visualize the [Ni(H2O)4(bis-pyridine)]n columns.

We expected that crystal structures 1-3 were good candidates for solid state transformations driven by temperature. The phosphinate moiety decomposes at around 300°C, a temperature comparable to thermally stable carboxylate based MOFs. We have also previously observed that the coordination polymers formed by bis-pyridines and phosphinates are generally crystalline and stable up to the decomposition temperature of bis-pyridines (250°C).23-26 Thermogravimetric analysis (TGA) of 1 shows
that the phase is stable up to 150°C (see Figure S2). The observed weight loss of 37.6% (35.8 Calcd.)
corresponds to the release of the four water molecules and the degradation of the bipy. Between 270°C
and 450°C, the diagram shows a new stability range that most likely corresponds to [Ni(pc₂p)]ₙ phase.
The temperature dependent X-ray diffraction (TD-XRD) experiment (see Figure S3) shows that 1 is
stable and crystalline up to 150°C. At higher temperature, only few broad peaks are observed and they
are attributed to the [Ni(pc₂p)]ₙ phase. In the case of 2, as shown in Figure 3a, the synthesized phase is
stable up to 90°C. The weight loss between 90°C and 140°C corresponds to the removal of four water
molecules (exp. 11.0%, calcld 11.6%). The successive loss corresponds to the burning of the bis-pyridine
ligand (exp. 39.2; calcld 41.1). The TD-XRD analysis between room temperature and 100°C (see Figure
3c) confirms the results of the TGA, i.e. the anhydrous [Ni(bpy-ene)(pc₂p)]ₙ phase, 2b, is a crystalline
phase. In addition, it is relatively stable at room temperature, as additional peaks of the pristine
compound are only seen after 17 hours in ambient conditions. Such behavior allowed us to readily
stabilize 2b to collect high-resolution powder X-ray diffraction (PXRD) data at 110 °C. Powder pattern
indexing led to unit cell dimensions close to their precursor’s, i.e., a = 10.656(8) Å, b = 12.941(8) Å, c =
26.22(1) Å, β = 94.52(6) °, V = 3604.8 Å³ [M₁₇ = 11.2, F₁₇ = 27(0.107, 60)], probable space group P
2/m. This result suggests that the full dehydration does not modify drastically the crystal structure of 2,
and the schematic arrangement of entities could obviously be preserved as illustrated in Figure 2. More
on the possible structure of 2b will be discussed below. The TGA of 3 is reported in Figure 3b. There is
no significant weight loss up to 90°C. In the range 90°C – 120°C, the corresponding weight losses
match with the removal of three water molecules (exp. 8.9%, Calcd 8.7%). Between 140°C and 160°C,
also the fourth water molecule is lost (exp. 2.7%, Calcd 2.9%). The anhydrous phase is stable up to
200°C. The additional weight loss corresponds to the removal of the bipyridine at higher temperature.
Finally, the [Ni(pc₂p)]ₙ phase is stable up to 450°C. A TD-XRD experiment, performed at a much lower
heating rate up to 160 °C, allowed to observe the corresponding dehydration stages at lower
temperatures, as shown in figure 3d. The [Ni(H₂O)(bpy-ene)(pc₂p)]ₙ phase, 3a, is obtained as a
crystalline phase between 60 and 100 °C. It transforms into the crystalline anhydrous [Ni(bpy-
ene)(pc₂p)]ₙ phase, 3b, which is observed till the end of the experiment at 160 °C. In this case ab-initio
indexing was not possible due to loss of crystallinity and broadening of many peaks. An additional in
situ XRD experiment was performed while cooling the sample in different atmospheres, to evaluate
whether 3b is stable in ambient conditions. This phase seems only sensitive to water, as it rehydrates
into its monohydrate parent 3a in air, while it is stable under pure N₂ (see Figure S3). Additionally,
phase 3a does not convert back into 3 when placed in contact with water.
Figure 3: (a) TG/DTA curve of compound 2; (b)TG/DTA curve of compound 3; (c) temperature dependent XRD experiment showing the dehydration of 2 and the slow re-hydration of 2b back to ambient(d); temperature dependent XRD experiment for 3.

We tried to dehydrate single crystals of 2 and 3 simply by heating a batch of crystals at 140°C for one night under vacuum. For 2, we did not obtain suitable crystals, while for 3 after the treatment, it was possible to collect and solve the structure of 3a by single crystal X-ray diffraction. As already pointed out, in air 3b spontaneously rehydrates into its monohydrate parent.
Figure 4. a) Fragment of the structures of 3a  b) Crystal packing of 3a. In this case, the green square represents the Nickel atom bonded to one water molecule.

In order to schematize the network, the same representation of Figure 2 for pc$_2$p, bipy and Ni(H$_2$O) was used, as well as the corresponding stick and ball models (hydrogen atoms are omitted). The 3D network of 3a is assembled using Ni and pc$_2$p (phenyl rings are omitted) in 1D sheets; the latter are connected by the bipyridine molecule. Ni(II) is still octahedrally coordinated, but three basal coordination sites are hereby occupied by oxygen atoms of three different pc$_2$p ligands and the fourth position is taken up by a water molecule (Figure 4a). The 1D pillars of [Ni(bipy)] are now connected by the pc$_2$p ligand. A new 1D [Ni(H$_2$O)(pc$_2$p)] chain is formed, as shown in Figure 4b. Strong hydrogen bonds are formed between the water molecules and the oxygen atoms of the diphosphinate groups not involved in the metal coordination (O-O distances = 2.71 Å). The 1D [Ni(bpy-ene)] pillars connect the 1D [Ni(pc$_2$p)] chains and the resulting structure is a 3D network with 3-connected (pc$_2$p ligand) and 5-connected (Nickel atom) nodes. Figure 5 shows the proposed mechanism of formation of 3a, focusing on the breaking and formation of coordination bonds that involve Ni and pc$_2$p, modeled upon the crystal structure of 3: removal of three water molecules from the Ni coordination sphere (Figure 5a to 5b) triggers reorganization of the hydrogen bonds network and every pc$_2$p molecule coordinates to three different Ni atoms (Figure 5b to 5c), thus leading to twisting of the pc$_2$p units and formation of the chains of Ni(pc$_2$p) held together by hydrogen bonds observed in 3a (Figure 5c to 5d).
Figure 5. Proposed mechanism for the phase transition leading from 3 to 3a. (a) Arrangement of Ni octahedra and pc$_2$p units in 3. (b) Residual coordination bonds and hydrogen bonds in 3 after removal of three water molecules per Ni atom. (c) Reorganization of hydrogen bonds and formation of new coordination bonds between pc$_2$p units and Ni atoms, accompanied by twisting of the pc$_2$p. (d) Final structure of 3a. Different colors are used to distinguish Ni atoms that end up belonging to different chains in 3a. Colour code: Ni atoms are represented in light blue and light gray, P atoms are represented in pink, C atoms are represented in black, O atoms are represented in red, N atoms are represented in blue, H atoms are represented in white. Hydrogen bonds are represented as red dashed lines. Newly formed coordination bonds are represented as dashed green lines in (c) and bold green lines in (d).

Substantial reorganization of the $\pi-\pi$ stacking interactions network takes place during the phase transition (Figure S4). 1, 2 and 3 all feature similar $\pi-\pi$ stacking interactions between the phenyl rings of adjacent pc$_2$p units, while bis-pyridines are not involved in any non-covalent interaction. In 3a this arrangement is disrupted and new interactions involving also bpy-ene are established. The phase transition does not involve breaking and formation of bonds between bpy-ene and Ni, however the [Ni(bpy-ene)] chains experience a significant distortion in 3a (Figure S5). The topological analysis reveals a 3,5T1 net, reported to be in the first 30 most frequent underline single net.\textsuperscript{52} Considering the
hydrogen bond between the uncoordinated oxygen atom of diphosphinate and the water molecule, the overall topology becomes fsc with a 4-connected (pc$_2$p ligand) and 6-connected (Nickel atom) nodes. This gives us some hints on the structure 3b. Likely, the uncoordinated oxygen atoms of the phosphinic ligands could displace the coordinated water molecule thus connecting to the Nickel atom and extending the connectivity into a 3D network.

Since it was not possible to obtain the crystallographic structure of 2b, we decided to investigate its spectroscopic and magnetic properties and to compare them with those of 2 and 3. UV-VIS spectra of 2 and 2b (see Figure S7) display similar features except for a blue shift of the peaks for 2b suggesting a similar coordination geometry in both cases. Unfortunately, no information could be obtained from EPR spectroscopy since compound 2b is EPR silent from room temperature down to 10 K probably due to an excessive zero field splitting, (ZFS). As a comparison, 2, 3 and 3a spectra have also been recorded at room temperature and 10 K. None of them show EPR transition at this frequency. The temperature dependence of the molar susceptibility product with the temperature, $\chi_M T$, for 2, shown in Figure S8, is consistent with that expected for a Ni (II) ion in an octahedral ligand field$^{33}$: $\chi_M T$ increases with temperature up to ca. 25 K and then remains constant at 1.39 emu.K.mol$^{-1}$ up to the highest measured temperatures. For 2b, the $\chi_M T$ versus T increases with the temperature until reaching a maximum at 5.5 K, it then decreases before reaching a constant value of 1.24 emu.K.mol$^{-1}$ from 50K to room temperature. As a comparison, 3b was also measured. The thermal variation of its $\chi_M T$ product undergoes a similar behavior with a maximum at 6.5 K. The low temperature maximum can be attributed to a weak ferromagnetic interactions through O-P-O bridges connecting Ni ions in the dimeric units, and to the large ZFS which characterizes Ni ions in octahedral geometry. The similarity of the room temperature $\chi_M T$ values between 2 and 2b indicates that the octahedral geometry is preserved upon the phase transition. A square planar coordination would result, indeed, in a diamagnetic behavior, so that this hypothesis can be definitely discarded. Moreover, the low temperature behavior of 2b, identical to 3b, suggests a similar metal environment in the two samples, where the Nickel atoms are surrounded by two nitrogen atoms from the pyridine rings and four oxygen atoms from four different pc$_2$p ligands.

We have presented a very special case in which quasi-similar CPs behave in very different ways, under the same heating conditions. To summarize, at first glance 1, 2 and 3 are almost the same compounds, having the same formula, the same coordination environment around the Ni metal atom and forming the same 1D network. A closer look reveals a different supramolecular arrangement for 1, 2 and 3 as well as a different calculated density. The change in behavior could be ascribed to the different length of the bridging unit of the two pyridine molecules. The N-N distances are 7.112(3), 9.390(2) and 9.436(4) Å.
for bipy, bpy-ane and bpy-ene in 1, 2, and 3, respectively. The two latter values have to be compared
with the equivalent distances of phosphorus atoms of two pc₂₂p in 2 and 3, i.e., 9.799(2) Å and 9.855(2)
Å respectively. With this in mind, bipy is clearly too short to allow the crystal arrangement shown by 3a
or the expected one for 2b and 3b. The identification of the partially hydrated phase 3a could be related
to the different flexibility of bpy-ane and bpy-ene. Bpy-ene preferably adopts a planar conformation,
owing to the conjugation of the two pyridine rings through the double bond. In 3a, one of the
crystallographically independent bpy-ene units is already significantly distorted and it is likely that 3b
demands even more distortion. This suggests that the system prefers to retain one water molecule
coordinated to each Ni atom instead of replacing it with a P-O group from a phosphinate unit. As a
matter of fact, 3b readily uptakes one water molecule when exposed to moist air, while 3a is stable over
a long period in the presence of water. In the case of 2, the ideal monohydrate phase 2a was probably
not isolated because the higher flexibility of bpy-ane molecule leads to preferential stabilization of
compound 2b.

These findings help us to critically review other transformations observed in previous papers such as the
transformation of the 1D MONT compound in 1D strip. In that example, the phosphinic ligand (pcp)
was linked to copper forming [Cu(pcp)]ₙ 1D columns. These columns remained stable during the
transformation while Cu-N bonds were broken and reformed. In the present work, we observed that the
[Ni(bis-pyridine)]ₙ columns remained the same while new Ni-O bonds were formed in the process. This
behavior could be related both to the different strength of the metal-ligand bonds in the two series of
compound but also the better chelating ability of pcp, compared to pc₂₂p, could have a certain importance
in the building up well stable [Cu(pcp)]ₙ columns.

Conclusions
In this paper, the structure and reactivity of three related 1D Ni-phosphinate CPs were studied. For the
three compounds, we have reported how the transformation of 1D coordination compounds in 3D ones
induced by the temperature took place. The different mechanisms involved in the formation of the 3D
coordination polymers in the case of two related class of ligand which differ only by a methylene group
(namely the pcp and the pc₂₂p ligands) were discussed. We found that pcp reacts first with the metallic
center and after the formation of a corner-like polymer the connection among the bipys occurred. In the
case of pc₂₂p, we have found that the affinity of the latter ligand is lower than the one of the bipys. In this
way, infinite 1D chains formed by [M(bipy)]ₙ are present in solution and the pc₂₂p connect them to build
the tridimensional structures. We can say that structures 1, 2 and 3 can be considered a sort of proto-
coordination polymers able to afford novel 3D structures upon heating which cannot be obtained by
direct synthesis. In our opinion, this study added important features to the comprehension of the
chemistry of CPs based on transition metal phosphinates.

**Experimental Section**

**Materials and Methods:** All reagents were analytical-grade commercial products and were used
without further purification. The p,p'-diphenylmethylenediphosphinic acid (H$_2$pcp) was prepared as
previously described.$^{54,55}$ Elemental analyses (C, H) were performed with an EA 1108 CHNS-O
automatic analyzer. Coupled thermogravimetric (TG) and differential thermal analysis (DTA)
measurements were performed using a Netzsch STA490C thermoanalyzer under a 20 mL min$^{-1}$ air flux
with a heating rate of 10 C min$^{-1}$. The IR spectra were recorded on Shimadzu IRAffinity-1S, equipped
with MIRacle PIKE ATR. DRS spectra were recorded in the reflectance mode by using an integrating
sphere on a Shimadzu UV-Visible Spectrophotometer UV-2600. BaSO$_4$ as a reference standard. The
spectra were converted to the corresponding absorption spectra by using the Kubelka–Munk equation.

*In situ* X-ray powder diffraction measurements were performed within an Anton Paar HTK 1200N
chamber attached to a Panalytical Empyrean powder diffractometer. (θ–θ Bragg–Brentano geometry)
working with the Cu-Kα radiation ($\lambda$ K$\alpha_1$ = 1.5406 Å, $\lambda$ K$\alpha_2$ = 1.5444 Å) selected with a flat multilayer
X-ray mirror (Bragg-Brentano HD®). Data were collected with a Pixel 1D silicon-strip detector, in the
useful angular range. Powder pattern indexing was carried out with the program DICVOL06.$^{56}$

**Synthesis of [Ni(H$_2$O)$_4$(bipy)·pc$_2$p]$_n$** 1: A solution of Ni(CH$_3$COO)$_2$·4H$_2$O (35 mg, 0.14mmol) in water
(10 ml) was added to a boiling water solution (60ml) of H$_2$pc$_2$p (43 mg, 0.14mmol) and bipy (22 mg,
0.14mmol). The resulting solution was boiled till green cubes started separating. Then the mixture was
held at ca. 80°C to complete the precipitation of the complex. The compound was filtered, washed with
water and dried in air, at room temperature. Yield 68% based on Nickel. Anal. Calc. for C$_{24}$ H$_{30}$ Ni O$_8$
N$_2$ P$_2$, mw=595.15gmol$^{-1}$: C, 48.44; N, 4.71; H, 5.08. Found: C, 48.42; N, 4.69; H, 5.15%.

**Synthesis of [Ni(H$_2$O)$_4$(bpy-ane)·pc$_2$p]$_n$** 2: A solution of Ni(CH$_3$COO)$_2$·4H$_2$O (35 mg, 0.14mmol) in
water (10 ml) was added to a boiling water solution (60ml) of H$_2$pc$_2$p (43 mg, 0.14 mmol) and bpy-ane
(26 mg, 0.14mmol). The resulting solution was boiled till green cubes started separating. Then the
mixture was held at ca. 80°C to complete the precipitation of the complex. The compound was filtered,
washed with water and dried in air, at room temperature. Yield 74% based on Nickel. Anal. Calc. for
C$_{26}$ H$_{34}$ Ni O$_8$ N$_2$ P$_2$, mw=623.20gmol$^{-1}$: C, 50.11; N, 4.50; H, 5.50. Found: C, 50.15; N, 4.45; H,
5.57%.

**Synthesis of [Ni(H$_2$O)$_4$(bpy-ene)·pc$_2$p]$_n$** 3: A solution of Ni(CH$_3$COO)$_2$·4H$_2$O (35 mg, 0.14mmol) in
water (10 ml) was added to a boiling water solution (60ml) of H$_2$pc$_2$p (43 mg, 0.14mmol) and bpy-ene
(26 mg, 0.14mmol). The resulting solution was boiled till green cubes started separating. Then the mixture was held at ca. 80°C to complete the precipitation of the complex. The compound was filtered, washed with water and dried in air, at room temperature. Yield63% based on Nickel. Anal. Calc. for C26 H32 Ni O8 N2 P2, mw=621.19gmol⁻¹: C, 50.27; N, 4.51; H, 5.19. Found: C, 50.30; N, 4.55; H, 5.28%.

**X-Ray Structure Determination:** The crystal data of compounds 1, 2, 3 and 3 are presented in Table 1. The single-crystal X-ray experiments were carried out on a CCD diffractometer with Mo Kα or Cu Kα radiation. The program CrysAlisCCD was used for data collection. Data reductions (including absorption corrections) were carried out with the program CrysAlis RED. The atomic coordinates were obtained by the direct methods in Sir97. Structure refinements were performed with SHELXL using the full-matrix least-squares method for all the available F² data. All the non-hydrogen atoms were refined anisotropically.

**Magnetic Characterization:** Magnetic susceptibility measurements were carried out using a Quantum Design MPMS SQUID magnetometer equipped with a 5 T magnet. Raw data were corrected for the diamagnetic contribution of the sample holder, and the intrinsic diamagnetism of the sample, estimated by Pascal’s constants. X-band (9.41GHz) EPR spectroscopic studies on microcrystalline powder samples placed in 4mm diameter quartz tubes were carried out at low temperatures using a Bruker E500 spectrometer equipped with an ESR900 (Oxford Instruments) continuous-flow ⁴He cryostat and a SHQ resonator

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**Note:** The authors declare no competing financial interest.

**ASSOCIATED CONTENT**
CCDC 1564548-1564551 contain the supplementary crystallographic data for this paper. These data can
be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing
data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union
Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Supporting information available

The supporting information is available free of charge on the ACS publication website at: DOI xxxx

Crystallographic tables containing structural information, bond lengths and angles for compounds 1, 2, 3 and 3a. TGA analysis for compound 1. Temperature dependent XRPD patterns for compound 1. Additional structural figures showing the H-bonds nets and the π – π stacking for compounds 2 and 3. IR and UV-VIS spectra are also reported.

REFERENCES

(6) Rather B., Zaworotko, M. J. A 3D metal-organic network, [Cu₂(glutarate)2(4,4'-bipyridine)], that exhibits single-crystal to single-crystal dehydration and rehydration Chem. Commun. 2003, 830-831.
(10) Habib, H. A.; Sanchiz, J.; Janiak, C. Mixed-ligand coordination polymers from 1,2-bis(1,2,4-triazol-4-yl)ethane and benzene-1,3,5-tricarboxylate: Trinuclear nickel or zinc secondary building units for three-dimensional networks with crystal-to-crystal transformation upon dehydration Dalton Trans. 2008, 1734-1744.


(41) Zhang, L-P.; Zhu, L-G. Monodentate function of the 4,4'-bipyridine that systematically occurs in the 4-sulfobenzoate manganese(II) complexes: syntheses, crystal structures, and properties CrystEngComm 2006, 8, 815-826.


(46) Wang, Q-W.; Li, X-M.; Han, J. Hydrothermal synthesis, crystal structure and magnetic properties of a cobalt(II) coordination polymer assembled by 4-sulfophthalate and 4,4′-bipyridine Jiegou Huaxue (Chin. J. Struct. Chem.) 2006, 25, 1369-1374


(47) Midollini, S.; Lorenzo-Luis, P.; Orlandini, A. Inorganic–organic hybrid materials of p,p′-diphenylmethylenediphosphinic acid (H₂pcp) with magnesium and calcium ions: Synthesis and characterization of [Mg(Hpcp)₂], [Mg(Hpcp)₂(H₂O)₄], [Mg(pcp)(H₂O)₃][H₂O], [Ca(Hpcp)₂] and [Ca(pcp)(H₂O)] complexes Inorg. Chim. Acta 2006, 359, 3275-3282


Same not the Same: Thermally-Driven Transformation of Nickel Phosphinate-Bipyridine 1D Chains into 3D Coordination Polymers
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Synopsis: Nickel phosphinate-bispyridine 1D chains undergo structural transformation into 3D networks upon heating. The transformation is influenced by the flexibility and the steric hindrance of the co-ligands.