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Factors Affecting the Conformational Modulation of Flexible Ligands in the Self-Assembly Process of Coordination Polymers: Synthesis, Structural Characterization, Magnetic Properties, and Theoretical Studies of $[Co(pda)(bix)]_n$, $[Ni(pda)(bix)(H_2O)]_n$, $[Cu(pda)(bix)_2(H_2O)_2]_n \cdot 8nH_2O$, $[Co_2(\mu\text{-}OH)(pda)(ptz)]_n \cdot nH_2O$, $[Co(hfipbb)(bix)_{0.5}]_n$, and $[Co(2,6\text{-}pydc)(bix)_{1.5}]_n \cdot 4nH_2O$

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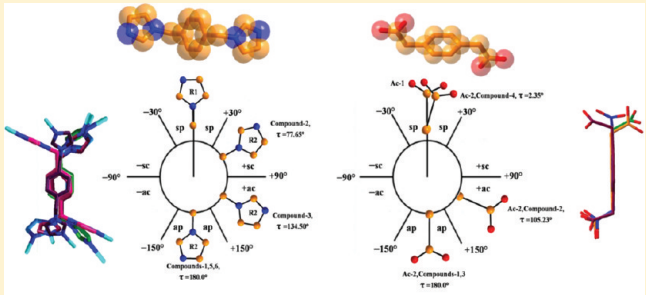
Supporting Information

ABSTRACT: Six new metal complexes with the formulae $[Co(pda)(bix)]_n$ (**1**), $[Ni(pda)(bix)(H_2O)]_n$ (**2**), $[Cu(pda)(bix)_2(H_2O)_2]_n \cdot 8nH_2O$ (**3**), $[Co_2(\mu\text{-}OH)(pda)(ptz)]_n \cdot nH_2O$ (**4**), $[Co(hfipbb)(bix)_{0.5}]_n$ (**5**), and $[Co(2,6\text{-}pydc)(bix)_{1.5}]_n \cdot 4nH_2O$ (**6**) have been synthesized by the reactions of Co(II), Ni(II), and Cu(II) salts with two flexible ligands 1,4-phenylenediaceticacid (H_2pda) and 1,4-bis (imidazole-1-ylmethyl)-benzene (bix) in the presence of coligands 5-(4-pyridyl) tetrazole (4-ptz), 4,4′(hexa-fluoroisopropylidene)bis-(benzoicacid) ($H_2hfipbb$), and 2,6-pyridine dicarboxylic acid (2,6-H_2pydc) and characterized by single crystal X-ray diffraction analysis, IR spectroscopy, and thermogravimetric (TG) analysis. Because of the coordination geometry around the metal ions and the diverse coordination modes of the flexible ligands in combination with the rigid and flexible coligands, the obtained complexes show diverse structures from a one-dimensional (1D) chain to three-dimensional (3D) coordination polymers. **1**, **4**, **5**, and **6** are Co(II) complexes in which Co(II) ions show tetrahedral coordination in **1**, trigonal bipyrimidal coordination in **4**, and octahedral coordination in **5** and **6**. Complexes **2** and **3** are respectively Ni(II) and Cu(II) complexes in which the metal ions are present in octahedral coordination geometries. Factors affecting the conformational change of the flexible ligands in the self-assembly process of coordination polymers, such as, coordination geometry around the metal ions and geometry of the coligands have been systematically studied. The rotation of the bonds $C(sp^3)-C(sp^2)$ and $C(sp^3)-N(sp^3)$ in H_2pda and bix ligands causes different conformations (cis, trans, gauche); these conformations have been studied by measuring the torsion angle. A comparative study between the torsion angle of the particular conformation of the ligands and coordination geometry of metal ion/geometry of the coligand has been undertaken. All the possible cis, trans, and gauche conformations of the flexible ligands have been obtained/observed in our complexes. Theoretical calculations were performed to determine the energies of the different conformations of the flexible ligands. The electronic properties of these complexes have also been investigated in the solid state at room temperature. Finally, the temperature-dependent magnetic studies for compounds **4** and **5** are described.



INTRODUCTION

Exploring the chemistry of micro- and mesoporous coordination polymers (CPs) or metal organic frameworks (MOFs), based on the self-assembly processes, is of great interest in modern inorganic chemistry because of their potential applications in gas storage, catalysis, nonlinear optics, separation, sensing, etc.[1] Designing of coordination polymers with specified properties remains an intriguing challenge to synthetic chemists, in terms of choosing both organic building units (OBUs) as well as metal ions.[2] A vast literature has been reported in the judicious selection of organic ligands in attaining the desirable topologies.[3] MOFs, based on rigid carboxylate linkers, have been widely studied and highly explored extensively by Yaghi and co-workers.[4] The combinations of carboxylate linkers along with N-donor linkers were also used to construct a wide variety of three-dimensional (3D) open framework materials with interesting sorption properties.[5] In contrast to the rigid ligands, the rational design of coordination polymers based on flexible ligands are quite interesting in terms of the self-assembly process and structure−property relationship.[6] Because of the conformational freedom of the flexible ligands, it results in formation of both discrete macrocylces and infinite polymeric structures; conversion

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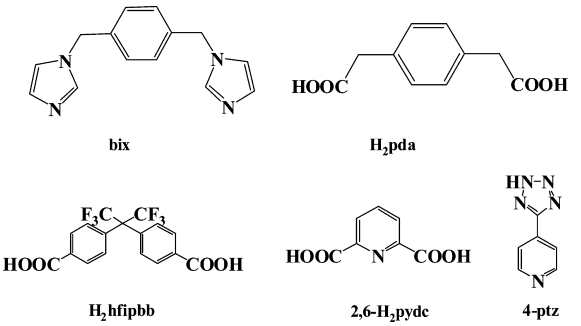
between these two types of structures (discrete and polymer) could also be achieved by the ring-opening isomerism.[7] Cao and his group studied and reviewed the coordination polymers based on flexible ligands.[8] The conformational freedom of flexible ligands offers the possibility to construct unpredictable and interesting coordination networks with useful properties. The final structures, based on flexible ligands, are subjected to several factors, such as synthetic conditions (temperature, pH, pressure, and solvents), coordination geometry of metal ions, geometrical disposition of donor sites, template molecules, and so on.[9] Thus, an investigation of the correlation between the subtle conformation of a flexible ligand and the topology of the coordination network formed is a challenging task for inorganic chemists, and it is necessary to check some properties of the resulting coordination polymers.

We have been focusing on the study of coordination polymers to evaluate the necessary concepts in the self-assembly process. Recently, we have demonstrated the effect of solvent molecules in directing the dimensionality of coordination networks from one-dimensional (1D) to 3D.[10] These studies give us practical experience in studying the assembly of coordination networks. 1,4-Benzenedicarboxylate (bdc^{2-}) is a well-known example of a principle rigid system among the carboxylates, and a similar analogue in the N-donor organic ligand is 1,4-bis(1-imidazolyl)benzene) (1,4-bdx); numerous coordination polymers have been reported to explore the binding modes of these ligands in the self-assembly processes.[11,12] The study of flexible analogues of these rigid systems would clarify the basic principles in the self-assembly process of coordination polymers compared to the rigid ligands. 1,4-Phenylenediaceticacid (H_2pda), and 1,4-bis (imidazole-1-ylmethyl)-benzene (bix) are such examples of flexible ligands that resemble the corresponding rigid ligands. Recently, we have reported both cis and trans conformations of the flexible phosphonate analogue (*p*-xylylenediphosphonic acid) with cobalt ion.[13] There are several reports on H_2pda with all the possible conformations of the ligand with and without using coligands.[14] Cao and co-workers demonstrated the conformation control of flexible H_2pda from trans to cis conformation by introducing a rigid auxiliary ligand 4,4′-bipyridine.[15] Shi and group reported a series of Zn(II) coordination complexes from isomeric phenylenediacetic acid (1,4-, 1,3-, 1,2-H_2pda) and dipyridyl ligands.[16] On the other hand, bix is another versatile flexible ligand, through which a wide variety of coordination polymers have been constructed, of which some of them exhibit unusual types of entanglement (e.g., rotaxane-like catenation).[17] The deviation and rotation of the $C(sp^3)-C(sp^2)$ bond in H_2pda with respect to the benzene ring causes disposition of (−COOH) groups in different directions. In the same way, $C(sp^3)-N(sp^3)$ bond in bix causes disposition of imidazole rings in different directions. Apart from the typical cis and trans conformations of the above said flexible ligands, there are some other conformations lying between these cis and trans conformations. These conformations can be described on the basis of torsion angle measurement of the rotation of the bonds $C(sp^3)-C(sp^2)$ and $C(sp^3)-N(sp^3)$ in H_2pda and bix, respectively.[18] On the basis of aforementioned considerations, we have chosen the flexible ligands H_2pda and bix to study the effect of the coordination geometry of the metal ions and the geometry of secondary ligands in modulating the conformations of the flexible ligands. Herein we report the synthesis and characterization of six coordination polymers $[Co(pda)(bix)]_n$ (**1**), $[Ni(pda)(bix)(H_2O)]_n$ (**2**), $[Cu(pda)(bix)_2(H_2O)_2]_n\cdot 8nH_2O$ (**3**), $[Co_2(\mu\text{-}OH)(pda)(ptz)]_n\cdot nH_2O$ (**4**), $[Co(hfipbb)(bix)_{0.5}]_n$ (**5**), and $[Co(2,6\text{-}pydc)(bix)_{1.5}]_n\cdot 4nH_2O$ (**6**). The conformational freedoms of these flexible ligands play a crucial role in the construction of the coordination networks varying from 1D to 3D. We have described the temperature-dependent magnetic studies for compounds **4** and **5**, considering the Co−Co distance in their crystal structures.

Scheme 1. Ligands Used in This Work



EXPERIMENTAL SECTION

Materials and Methods. All the chemicals were received as reagent grade and used without any further purification. The ligands bix and 4-ptz were prepared according to the literature procedures.[19] Elemental analyses were determined by a FLASH EA series 1112 CHNS analyzer. Infrared spectra of solid samples were obtained as KBr pellets on a JASCO-5300 FT-IR spectrophotometer. Thermogravimetric analyses were carried out on an STA 409 PC analyzer, and corresponding masses were analyzed by a QMS 403 C mass analyzer, under a flow of N_2 gas with a heating rate of 5 °C min^{-1} in the temperature range of 30−1000 °C. Powder X-ray diffraction patterns were recorded on a Bruker D8-Advance diffractometer using graphite monochromated $CuK_{\alpha 1}$ (1.5406 Å) and $K_{\alpha 2}$ (1.54439 Å) radiations. The electronic absorption spectra were recorded on a Cary 100 Bio UV−visible spectrophotometer at room temperature. Magnetic susceptibilities were measured in the temperature range of 2−300 K on a Quantum Design VSM-SQUID. The energy calculations for the bix and pda^{2-} in the crystal structures have been performed by using B3LYP with 6-311g** basis set from the XMol (*.xyz) files of the compounds. All the compounds were synthesized in 23 mL Teflon-lined stainless vessels (Thermocon, India).

Synthesis of $[Co(pda)(bix)]_n$ (1). A mixture of $CoCl_2\cdot 6H_2O$ (0.12 g, 0.5 mmol), H_2pda (0.097 g, 0.5 mmol), and bix (0.12 g, 0.5 mmol) was dissolved in 10.0 mL of distilled water. The pH of the reaction mixture was adjusted to 6.0 by addition of 1 M NaOH solution. Consequently, the resulting mixture was stirred for 30 min and transferred to a 23 mL Teflon-lined stainless vessel, which was sealed and heated at 180 °C for 72 h, and the reaction system was cooled to room temperature over 48 h to obtain purple crystals. Yield: 49% (based on Co) Anal. Calcd. for $C_{24}H_{22}CoN_4O_4$: C, 58.90; H, 4.53; N, 11.44. Found: C, 59.10; H, 4.25; N, 11.68. IR (KBr pellet, cm^{-1}): 3792, 3126, 2916, 1618, 1585, 1523, 1365, 1275, 1086, 1024, 932, 788, 740.

Synthesis of $[Ni(pda)(bix)(H_2O)]_n$ (2). The same synthetic procedure was used to synthesize **2** as that for **1** except $Ni(NO_3)_2\cdot 6H_2O$ (0.14 g, 0.5 mmol) was used instead of $CoCl_2\cdot 6H_2O$ to obtain light green crystals. Yield: 45% (based on Ni) Anal. Calcd. for $C_{24}H_{24}NiN_4O_5$: C, 56.84; H, 4.76; N, 11.04. Found: C, 56.70; H, 4.84; N, 11.21. IR (KBr pellet, cm^{-1}): 3393, 2966, 1558, 1518, 1375, 1261, 1232, 1086, 1024, 941, 800, 721.

Synthesis of $[Cu(pda)(bix)_2(H_2O)_2]_n\cdot 8nH_2O$ (3). The same synthetic procedure was used to synthesize **3** as that for **1** except

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$CuCl_2·2H_2O$ (0.085 g, 0.5 mmol) was used instead of $CoCl_2·6H_2O$ to obtain blue block crystals. Yield: 48% (based on Cu) Anal. Calcd. for $C_{38}H_{56}Cu\ N_8O_{14}$: C, 50.02; H, 6.18; N, 12.28. Found: C, 50.25; H, 6.02; N, 12.10. IR (KBr pellet, cm^{-1}): 3400, 3113, 1651, 1574, 1521, 1450, 1358, 1251, 1138, 1109, 1024, 947, 850.

Synthesis of $[Co_2(\mu\text{-OH})(pda)(ptz)]_n·nH_2O$ (4). A mixture of $Co(OAc)_2·4H_2O$ (0.099 g, 0.4 mmol), H_2pda (0.038 g, 0.2 mmol), and 4-ptz (0.029 g, 0.2 mmol) was dissolved in 10.0 mL of distilled water and the pH of the reaction mixture was adjusted to 4.72 by 0.5 M NaOH. Then the resulting mixture was stirred for 30 min and transferred to 23 mL Teflon-lined stainless vessel, sealed, and heated at 180 °C for 72 h and then cooled to room temperature over 48 h to obtain red block crystals. Yield: 63% (based on Co) Anal. Calcd. for $C_{16}H_{13}Co_2N_5O_6$: C, 39.28; H, 2.67; N, 14.31. Found: C, 39.12; H, 2.38; N, 14.72. IR (KBr pellet, cm^{-1}): 3568, 2916, 2845, 1591, 1412, 976, 760, 717, 555.

Synthesis of $[Co(hfipbb)(bix)_{0.5}]_n$ (5). To a mixture of $CoCl_2·6H_2O$ (0.12 g, 0.5 mmol), bix (0.12 g, 0.5 mmol), and H_2hfipbb (0.19 g, 0.5 mmol), 10.0 mL of distilled water and 1.0 mL of MeOH were added and the pH was adjusted to 5.2 by adding 0.5 M NaOH. The resulting reaction mixture was stirred for more than 2 h and transferred to a 23 mL Teflon-lined stainless vessel, sealed, and heated at 180 °C for 72 h and then cooled to room temperature over 48 h to obtain red block crystals. Yield: 59% (based on Co) Anal. Calcd. for $C_{24}H_{15}CoN_2F_6O_4$: C, 50.72; H, 2.66; N, 4.92. Found: C, 50.98; H, 2.42; N, 5.01. IR (KBr pellet, cm^{-1}): 3454, 3140, 2924, 1626, 1523, 1410, 1253, 1172, 1105, 1020, 929, 842, 781, 723, 652.

Synthesis of $[Co(2,6\text{-pydc})(bix)_{1.5}]_n·4nH_2O$ (6). To a mixture of $CoCl_2·6H_2O$ (0.12 g, 0.5 mmol), bix (0.12 g, 0.5 mmol), and 2,6-H_2pydc (0.083 g, 0.5 mmol), 10.0 mL of distilled water and 1.0 mL of MeOH were added and the pH was adjusted to 6.0 by adding 0.5 M NaOH. The resulting reaction mixture was stirred for more than 2 h, and the clear solution was transferred to a 23 mL Teflon-lined stainless vessel, sealed, and then heated to 160 °C for 72 h and cooled to room temperature over 48 h to obtain red plate-like crystals. Yield: 65% (based on Co) Anal. Calcd. for $C_{28}H_{32}CoN_7O_8$: C, 51.46; H, 4.93; N, 15.00. Found: C, 51.20; H, 5.10; N, 14.75. IR (KBr pellet, cm^{-1}): 3441, 3121, 2199, 1628, 1587, 1521, 1444, 1425, 1359, 1284, 1234, 1182, 1086, 1028, 941, 844.

Single Crystal X-ray Structure Determination of the Compounds 1–6. Single crystals suitable for structural determination of all the compounds (**1**–**6**) were mounted on a three circle Bruker SMARTAPEX CCD area detector system under Mo–Kα (λ = 0.71073A) graphite monochromated X-ray beam, crystal-to-detector distance of 60 mm, and a collimator of 0.5 mm. The scans were recorded with an ω scan width of 0.3°. Data reduction was performed using SAINTPLUS,[20a] empirical absorption corrections using equivalent reflections were performed using the program SADABS,[20b] and structure solution using SHELXS-97[20c] and full-matrix least-squares refinement using SHELXL-97[20d] for the above compounds. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the C atoms were introduced on calculated positions and were included in the refinement riding on their respective parent atoms. Attempts to locate the hydrogen atoms for the solvent water molecules in the crystal structure of compounds **3**, **4**, and **6** failed. However, no attempts were made to fix these atoms on their parents. Co atoms in the crystal structure of **4** are refined with occupancy each 0.95, and several attempts were made to improve the occupancy and the best value is taken considering the convergence of the refinement. Crystal data and structure refinement parameters for all the compounds (**1**–**6**) are summarized in Table 1, and selected bond lengths and bond angles are presented in section 5 in Supporting Information. Topological analysis of the compound **1** was performed by using the TOPOS software.[20e]

Table 1. Crystal Data and Structural Refinement Parameters for Compounds 1–6

	1	2	3
empirical formula	$C_{24}H_{22}N_4O_4Co$	$C_{24}H_{24}N_4O_5Ni$	$C_{38}H_{56}N_8O_{14}Cu$
formula weight	494.01	507.18	912.46
T (K)/λ (Å)	298(2), 0.71073	298(2), 0.71073	298(2), 0.71073
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	6.892(6)	8.655(4)	8.370(4)
b (Å)	8.561(7)	10.949(6)	10.357(5)
c (Å)	18.950(16)	23.799(12)	13.037(6)
α (°)	96.295(10)	90.00	101.575(6)
β (°)	98.064(10)	100.017(7)	90.785(6)
γ (°)	103.275(10)	90.00	101.798(7)
volume (Å^3)	1065.80(16)	2221.0(19)	1082.0(9)
Z, ρ_{calcd} (g cm^{-3})	2, 1.539	4, 1.517	1, 1.400
μ (mm^{-1}), F(000)	0.846/510	0.919/1056	0.579/481
goodness-of-fit on F^2	1.132	1.069	1.083
R_1/wR_2 [$I > 2\sigma(I)$]	0.0565/0.1341	0.0331/0.0835	0.0433/0.1031
R_1/wR_2 (all data)	0.0635/0.1392	0.0385/0.0865	0.0475/0.1057
largest diff peak/hole (e Å^{-3})	0.621/−0.579	0.479/−0.176	0.272/−0.201
	4	**5**	**6**
empirical formula	$C_{16}H_{13}N_5O_6Co_2$	$C_{24}H_{15}F_6N_2O_4Co$	$C_{28}H_{32}N_7O_8Co$
formula weight	489.17	568.31	653.54
T (K)/λ (Å)	298(2), 0.71073	298(2), 0.71073	298(2), 0.71073
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$C2/c$	$P\bar{1}$
a (Å)	9.0096(9)	27.375(6)	10.122(3)
b (Å)	20.558 (2)	7.277(15)	12.159(4)
c (Å)	9.7353(10)	24.644(5)	13.553(4)
α (°)	90.00	90.00	91.707(5)
β (°)	100.547(2)	106.240(2)	109.504(5)
γ (°)	90.00	90.00	102.552(5)
volume (Å^3)	1772.7(3)	4731.4(16)	1525.2(8)
Z, ρ_{calcd} (g cm^{-3})	4, 1.833	8, 1.602	2, 1.423
μ (mm^{-1}), F(000)	1.919, 984	0.810, 2288	0.623, 680
R_1/wR_2 [$I > 2\sigma(I)$]	0.0729/0.1894	0.0372/0.0912	0.0651/0.1456
R_1/wR_2 (all data)	0.0182/0.1930	0.0447/0.0942	0.0804/0.1543
largest diff peak/hole (e Å^{-3})	2.259/−0.712	0.802/−0.297	0.610/−0.266

RESULTS AND DISCUSSION

Synthesis. All the compounds **1**–**6** were synthesized by conventional hydrothermal procedures by employing divalent metal salts and the appropriate ligands as mentioned in Scheme 1. The infrared spectra of all the compounds are consistent with their single crystal structures. The aromatic ring stretching frequencies of the pda^{2-} and bix ligands are present in the range of ~1600 to 1200 cm^{-1}. The asymmetric and symmetric stretching frequencies of the C–O stretching modes of the dicarboxylate ligands are present as strong bands at 1585 and 1523 cm^{-1} (**1**), 1558 and 1518 cm^{-1} (**2**), 1574 and 1521 cm^{-1} (**3**), 1591 and 1412 cm^{-1} (**4**), 1523 and 1410 cm^{-1} (**5**), and 1587 and 1521 cm^{-1} (**6**). The aliphatic C–H stretchings of the $-CH_2$ group in all the compounds are present in the range of 2800 to 3000 cm^{-1}. The bands arising from the O–H stretching modes of the coordinated and uncoordinated water

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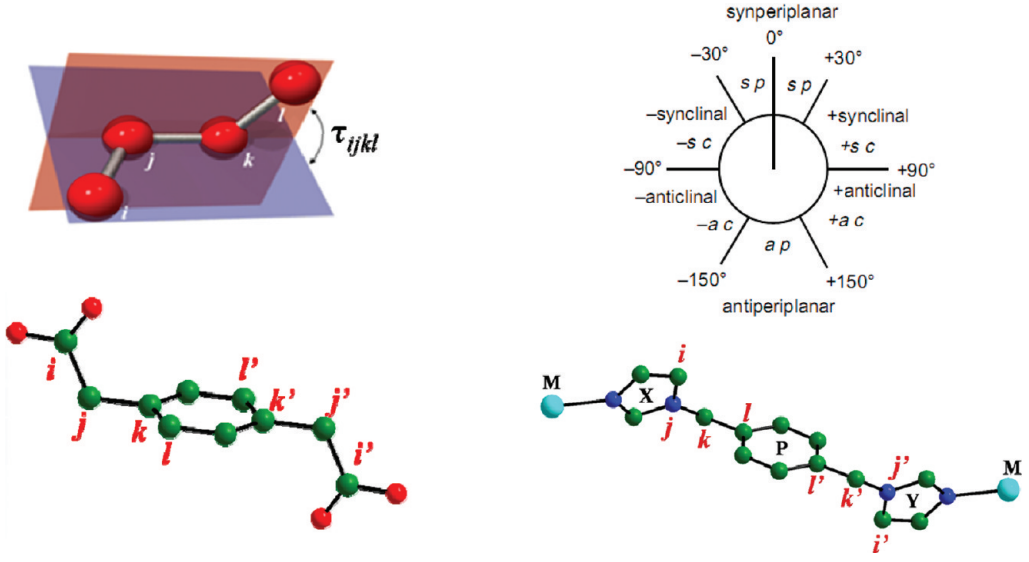
Scheme 2



molecules are observed in the range of 3300 cm^{-1}. The identities of the compounds **1**−**6** are further confirmed by structure solution from single crystal X-ray diffraction. The rotation of the $C(sp^3)-C(sp^2)$ and $C(sp^3)-N(sp^3)$ bonds in the pda^{2-} and bix ligands respectively are explained on the basis of the torsion angle as described below.

Definition of Torsion Angle. Torsion angle (τ) in the chain of the vectors (atoms) *i*, *j*, *k*, *l* can be defined as the dihedral angle between the plane of vectors containing *i*, *j*, *k* and the plane containing *j*, *k*, *l* (Scheme 2). In a Newman projection, the torsion angle is the angle (having an absolute value between 0° and 180°) between the bonds of two specified groups, one from the atom nearer (proximal) to the observer and the other from the further (distal) atom. The torsion angle between the atoms *i* and *l* is then considered to be positive if the bond *i*−*j* is rotated in a clockwise direction through less than 180° in order that it may eclipse the bond *k*−*l*; a negative torsion angle requires rotation in the opposite sense. Stereochemical arrangements corresponding to torsion angles between 0° and 180° based on the direction of the rotation are shown in Scheme 2.

By locating the *i*, *j*, *k*, *l* atoms in the dipodal flexible ligands pda^{2-} and bix at the flexible group ($-CH_2-$), the torsion angles are measured and the conformations of the ligands are explained. Three different types of torsion angles for both pda^{2-} and bix ligands are considered to measure the skewing of the acetate and imidazole groups, in which $\tau_1(ijkl)$ and $\tau_2(l'k'j'i')$ are calculated to measure the twist of acetate and imidazole groups from the mean phenyl ring plane. $\tau_3(ijj'i')$ and $\tau_3(jkk'j')$ are calculated to measure the twist with respect to each other acetate and imidazole rings, respectively. Torsion angle τ_3 gives the information of the particular conformation of the ligand (such as cis, trans, and gauche or skew) as shown in Scheme 2.

Description of Crystal Structures. *$[Co(pda)(bix)]_n$ (**1**).* Compound **1** crystallizes in triclinic space symmetry $P\bar{1}$. The asymmetric unit of **1** consists of one independent Co(II) ion, one pda^{2-} anion, and one bix ligand. As shown in Figure 1a, each Co(II) ion in **1** is four coordinated with distorted tetrahedral geometry composed of two carboxylic oxygen atoms from two pda^{2-} anions (Co−O = 2.001(3) and 1.996(3) Å) and two nitrogen atoms from two bix ligands (Co−N = 2.061(3) and 2.024 (3) Å). pda^{2-} acts as a bidentate ligand with coordination mode μ_1-η^1:η^0 and coordinates to two cobalt atoms in a well-known trans configuration, with an antiperiplanar torsion angle of 180° and a separation of 12.80 Å between two cobalt atoms. A bidentate bix ligand coordinates to two cobalt atoms in a usual trans configuration (τ = 180°) and connects the cobalt atoms with a separation of 15.09 Å. The connectivity of the pda^{2-} and the bix ligands through the Co-tetrahedra forms meso-helices as shown in Figure 1b. The overall structure is composed by tetrahedral Co polyhedra linked by the linkers bix and pda^{2-} to form a 3D interpenetrated structure with a uniform pore size. In the dual ligand system containing carboxylate and N-donor ligands, various combinations involving flexible and rigid analogues based on phenylene spacers have been reported. Among those well-known combinations such as rigid carboxylate, rigid N-donor (1,4-H_2bdc, 1,4-bdx),[21] rigid carboxylate, flexible N-donors (1,4-H_2bdc, bix)[22] are studied. In the present system, the combination flexible carboxylate and flexible N-donor (H_2pda, bix) has been studied. Thus, the combination of flexible carboxylate and flexible N-donor ligand gives rise to a 3D porous coordination polymer with an approximate pore size of 15 × 15 Å (Figure 1c). Usually, long, rigid ligands result in interpenetration and decrease the pore sizes to a large extent.[23] In compound **1**, the combination of long flexible ligands results in a 3D framework; the flexibility of the ligands minimizes the interpenetration to give considerably uniform pore sizes.

To better understand the 3D structure of **1**, Co(II) ion in the tetrahedral coordination can be described as a four connected node, since it links two pda^{2-} ligands and two bix ligands. Each pda^{2-}/bix ligand is considered as a connector between two metal ions. Topological analysis of this framework with TOPOS software reveals a 4-fold interpenetrated diamond-type (dia 6^6 topology) structure. Such connectivity repeats infinitely to give the 3D framework of **1** as schematically shown in Figure 1d.

*$[Ni(pda)(bix)(H_2O)]_n$ (**2**).* X-ray diffraction analysis of compound **2** reveals that the asymmetric unit consists of one crystallographically independent Ni(II) center. As shown in Figure 2a, the six-coordinated Ni(II) center [NiN_2O_4] shows a distorted octahedral geometry with three carboxylate oxygen

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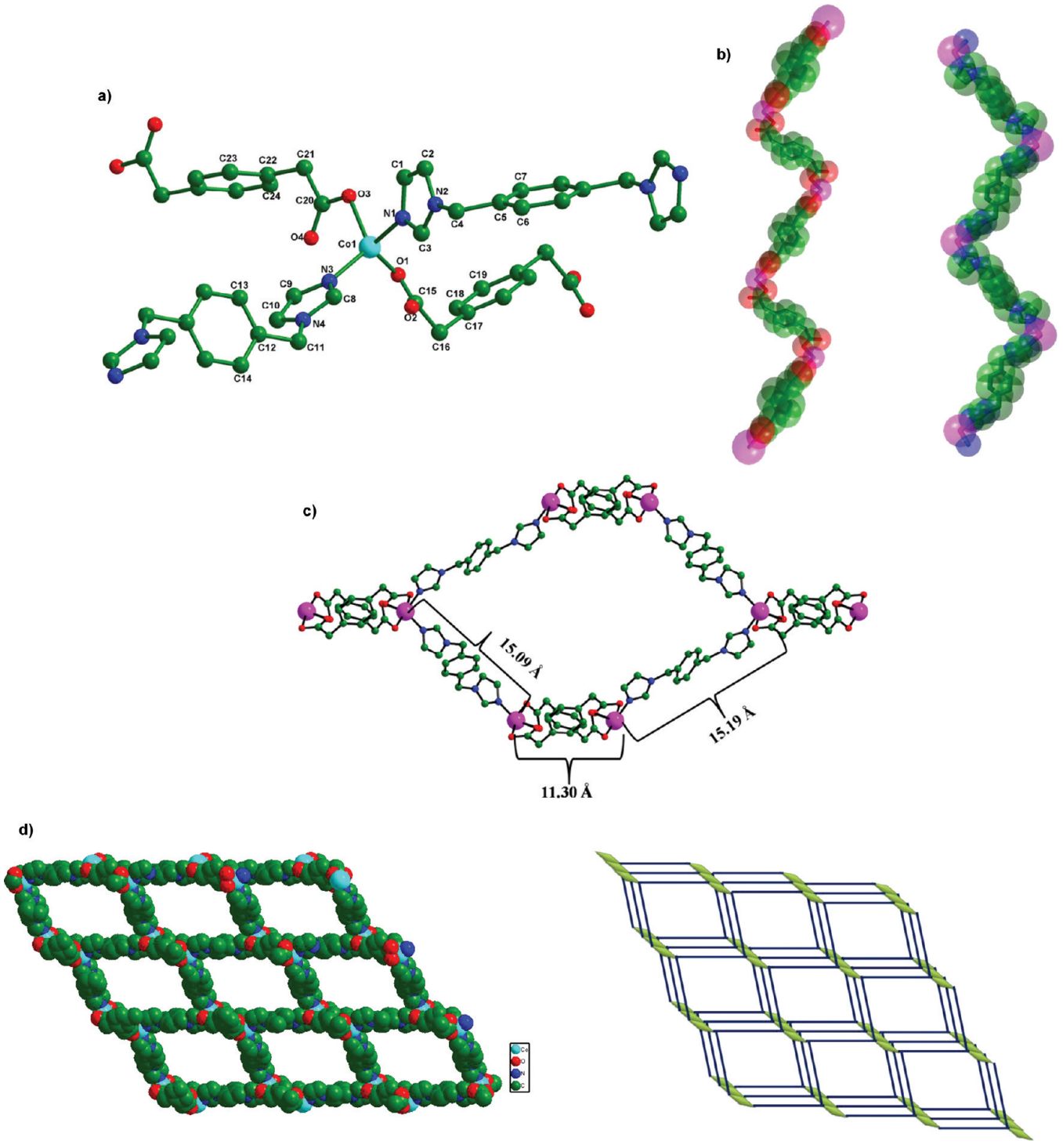

Figure 1. (a) Coordination environment around the Co^{II} ion in **1** with hydrogen atoms omitted for clarity. (b) Meso helices constructed by the pda^{2-} and bix ligands. (c) 3D framework of **1** illustrating the dimensions of the pore sizes. (d) 4-fold interpenetrated diamond net and its schematic representation.

donors (O1, O2, O3) from two different pda^{2-} ligands, one oxygen donor O5 from water molecule, and two nitrogen donors (N2, N3) from two different bix ligands. Complex **2** is an extended 1D chainlike structure consisting of two meso chains: chain-A, constituted by pda^{2-} ligands, and chain-B, constituted by bix ligands, as shown in Figure 2b. Each pda^{2-} ligand in chain-A is bidentate ligand which adopts μ_2-bridging mode with one carboxylate group in a μ_1-η^1:η^1 chelating mode and the other in a μ_1-η^1:η^0 monodentate mode. Furthermore, the acetate side chains are twisted with respect to the aromatic ring by various extents, in which arm-A (denoted by C16−C15) shows an antiperiplanar torsion angle of 174.63° (through C22−C17−C16−C15) and arm-B (denoted by C24−C23) exhibits an anticlinal torsion angle of −70.30° (through C19−C20−C24−C23). The two acetate groups twisted with respect to each other by an anticlinal torsion angle of 105.23° (through C16−C15−C24−C23), which is a gauche conformation of pda^{2-} ligand (Table 3). The pda^{2-}

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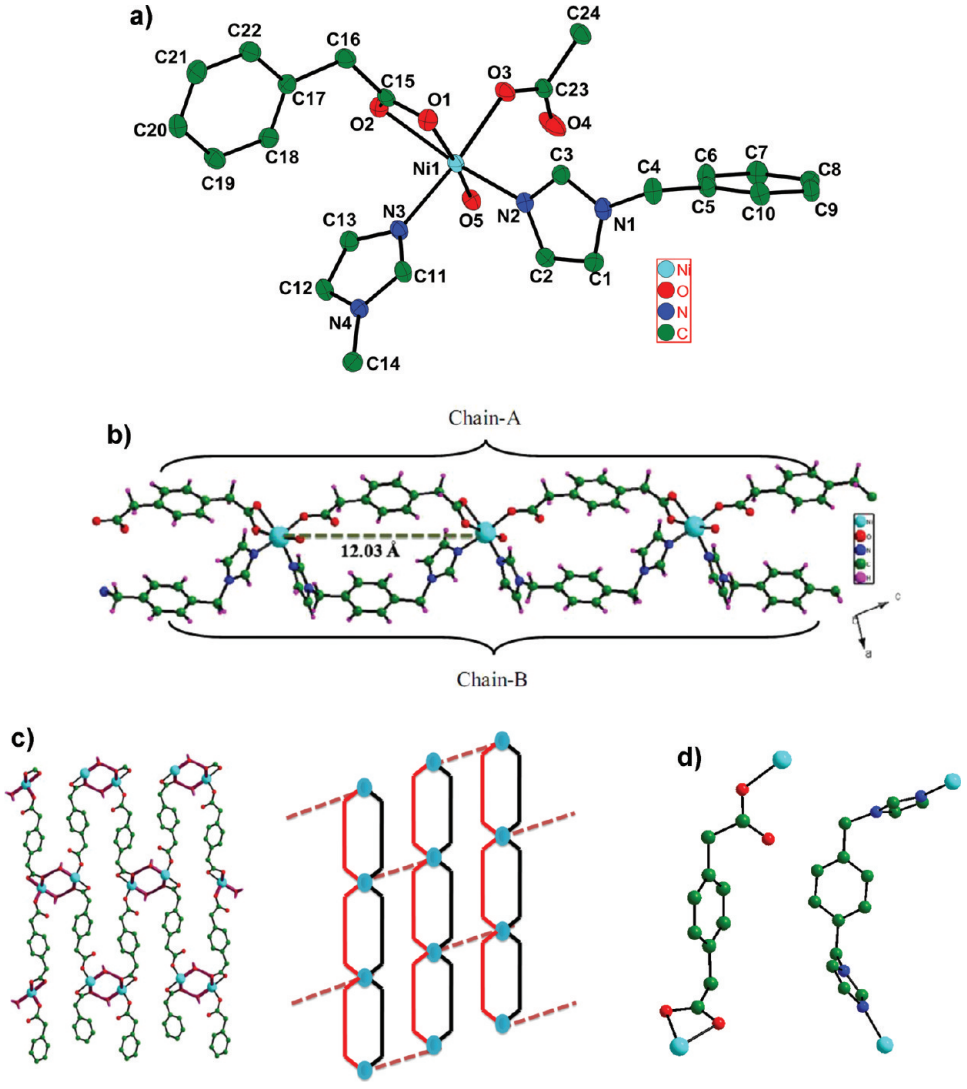

Figure 2. (a) Thermal ellipsoid plot of **2**. (b) 1D double chains constituted by pda^{2-} and bix ligands. (c) 2D supramolecular network formed due to hydrogen bonding and its schematic representation. (d) Gauche conformations of pda^{2-} and bix ligands.

along the chain separates the two Ni(II) centers with a distance of 12.03 Å, and the Ni−Ni−Ni angle through the pda^{2-} ligand is almost 180°. In chain-B the exo-bidentate ligand bix coordinates to Ni centers through a nitrogen donor, and the bix ligand twists their imidazole rings to different extents, in order to meet the coordination requirements imposed by the pda^{2-} ligand at the Ni octahedron. The dihedral angles between the imidazole ring planes and the least-squares plane of the phenyl group are 82.72° and 83.32°, respectively, and the two imidazole groups are twisted around each other by an synclinal torsion angle of 77.65° (through N1−C4−C14−N4). The bidentate bix molecules twist their imidazole rings to 77.65° to establish a physical bridge between Ni centers with a separation of 12.03 Å (Table 4), as imposed by the pda^{2-} ligand through chain-A. The two chains-A and -B constitute a 1D double-chain structure with a 25-membered ring between two metal centers. Because of coordination of the aqua ligand on the apical site of the Ni-octahedra, pda^{2-}, bix ligands modulate their conformations in order to meet the coordination requirements at the Ni(II)-octahedra. The adjacent double chains are linked via hydrogen bonding interactions with the aid of the water molecule and the carboxylate oxygen (O2) to form an eight-membered ring (Table 2) resulting in a two-dimensional (2D) network (Figure 2c). It must be remarked that in the crystal structure of **2**, both flexible ligands (pda^{2-} and bix) adopt gauche conformations apart from the regular trans and cis conformations to meet the coordination requirements of the metal atom (Figure 2d).

*$[Cu(pda)(bix)_2(H_2O)_2]_n \cdot 8nH_2O$ (**3**).* Compound **3** crystallizes in triclinic space group $P\bar{1}$. The repeating unit consists of one $[Cu(bix)_2(H_2O)_2]^{2+}$ cation, one pda^{2-} anion, and four lattice water molecules. The Cu(II) ion locates on a symmetry center and is coordinated by four nitrogen atoms from four different bix ligands in a basal plane and two oxygen atoms from two aqua ligands arranged trans to each other on the apical coordination sites to furnish an octahedral geometry (Figure 3a). The repeating unit $[Cu(bix)_2(H_2O)_2]^{2+}$ extends to 1D double-chain structure, in which the anion pda^{2-} occupies the void space created between two metal centers in the double chain (Figure 3b). Each constituent chain of the double chain is constructed by linking the two Cu(II) ions with the bidentate bix ligands with a separation of 13.03 Å. The bix ligand twists its imidazolyl moieties with respect to each other to an anticlinal torsion angle of 134.50°(through N2−C4−C8−N4), and the

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Table 2. Geometrical Parameters of the C−H···O and O−H···O Hydrogen Bonds (Å, °) Involved in Supramolecular Networks of Compounds 2, 3, and 6[a]

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
Compound **2**				
C(14)−H(14B)···O(4)#1	0.97	2.32	3.236(3)	156.6
C(4)−H(4A)···O(1)#2	0.97	2.34	3.259(3)	158.6
C(10)−H(10)···O(1)#2	0.93	2.78	3.542(3)	139.5
O(5)−H(5A)···O(2)#3	0.87(3)	1.86(3)	2.721(2)	172(3)
Compound **3**				
O(3)−H(3A)···O(2)#1	0.82(3)	1.95(3)	2.770(3)	174(3)
O(6)−H(6A)···O(5)#4	0.90(9)	1.90(9)	2.781(7)	166(8)
C(2)−H(2)···O(6)#5	0.93	2.61	3.388(6)	140.9
C(5)−H(5)···O(1)#6	0.93	2.43	3.323(3)	162.0
Compound **6**				
C(13)−H(13)···O(1)#6	0.93	2.68	3.515(6)	149.7
C(14)−H(14)···O(7)#7	0.93	2.46	3.306(7)	150.6
C(10)−H(10)···O(5)#4	0.93	2.53	3.384(7)	152.5
C(8)−H(8)···O(8)#8	0.93	2.65	3.556(6)	163.6
C(19)−H(19)···O(8)#9	0.93	2.49	3.344(6)	153.2
C(20)−H(20)···O(7)#8	0.93	2.45	3.282(8)	149.4
C(4)−H(4B)···O(6)#8	0.97	2.53	3.447(7)	158.7
C(1)−H(1)···O(6)#8	0.93	2.77	3.524(6)	138.6
O(6)−H(6A)···O(1)#4	0.95(6)	2.20(7)	2.851(6)	125(5)
O(8)−H(8B)···O(4)#8	0.92(7)	1.86(7)	2.774(5)	171(6)
O(8)−H(8A)···O(3)#10	0.74(6)	2.15(6)	2.822(5)	152(6)
O(7)−H(7A)···O(8)#3	0.89(6)	2.05(7)	2.935(7)	172(6)

[a]Symmetry transformations used to generate equivalent atoms. #1 $-x+1, -y+1, -z$. #2 $-x+1, -y, -z$. #3 $-x, -y+1, -z$. #4 $-x+1, -y, -z+1$. #5 $x-1, y, z-1$. #6 $x-1, y, z$. #7 $-x, -y, -z+1$. #8 $-x+1, -y+1, -z+1$. #9 $-x+2, -y+1, -z+1$. #10 $x, y, z-1$. D = donor; A = acceptor.

angles between the planes of the imidazole rings and the plane of phenylene group are 83.65° and 77.0°, respectively (Table 4). In the anion pda^{2-}, both the acetate side chains are twisted with respect to each other by an antiperiplanar torsion angle of 180.0° (denoted by C15−C16−C16−C15) exhibiting a typical trans conformation (Table 3). The existence of isolated pda^{2-} ligand as anion, apart from the Cu(II)-octahedron, is probably the factor for the bix ligand to adopt the gauche conformation with an anticlinal torsion angle apart from the regular trans and cis conformations. From the crystal packing diagram, it can be seen that the cationic chains and pda^{2-} anions are connected by the classical hydrogen bonds between the coordinated aqua ligands of cation, the carboxylate oxygen atoms of anion, and the lattice water molecules (Table 2). A hydrogen bonded eight-membered ring of type $R^4_2(8)$ has been formed with the assistance of the two coordinated aqua ligands (O3) and two carboxylate oxygen atoms (O2). This synthon $R^4_2(8)$ connects the two adjacent cationic chains along the *ac* plane and two pda^{2-} anions along the *b*-axis resulting in the 2D supramolecular network. Another ring of type $R^2_2(4)$ has been formed with the assistance of two water molecules (O6); this synthon connects the two pda^{2-} anions along the crystallographic *ac* plane with the help of lattice water molecule (O5) and carboxylate oxygen (O1) (Figure 3c).The overall supramolecular interactions result in a 3D supramolecular network as shown in Figure 3d (green color network due to bix and yellow color network due to pda^{2-}). Interestingly, in the crystal structure of complex **3**, the anion pda^{2-} templates the formation of cationic chains of $[Cu(bix)_2(H_2O)_2]_n^{2n+}$ without involving the coordination to the metal ion. The conformational freedom of the ligand bix allows it to twist its imidazole rings in order to meet the geometrical requirements imposed by the pda^{2-} anion.

*$[Co_2(\mu\text{-}OH)(pda)(ptz)]_n \cdot nH_2O$ (**4**).* As shown in Figure 4a, the asymmetric unit in the crystal structure of compound **4** (space group $P2(1)/n$) consists of two crystallographically independent Co(II) ions bridged by a hydroxyl group, one pda^{2-} anion, ptz^{1-} anion, and a lattice water molecule. Co1 is present in tbp geometry, defined by two oxygen atoms (O2, O5) from two different pda^{2-} anions, one μ_2-OH (O1) in the basal plane and two nitrogen donors (N2, N5) from two different ptz^{1-} anions (one from the tetrazole ring and another from the pyridine ring of ptz) in the apical positions. Another cobalt atom Co2 is also present in tbp geometry defined by two oxygen atoms (O3, O4) from two different pda^{2-} anions, one μ_2-OH (O1) in the basal plane and two nitrogen donors (N1, N4) from two different ptz^{1-} anions (both from the tetrazole rings). Each pda^{2-} anion coordinates to four Co(II) atoms with μ_2-η^1:η^1 bridging mode on either side in a typical cis conformation to form a molecular box (Figure 4b). Both acetate side chains in the pda^{2-} twist with respect to each other with a synperiplanar torsion angle of 2.30° (slight deviation of torsion angle for cis conformation) viewed through C1−C2−C9−C10. Furthermore, the acetate chains twist with respect to the phenylene ring to various extents, in which arm-A (denoted by C1−C2) shows an anticlinal torsion angle of −77.27° (through C1−C2−C3−C4) and arm-B (denoted by C10−C9) exhibits an anticlinal torsion angle of 101.92° (through C10−C9−C6−C7) (Table 3). The pda^{2-} coordination constitutes an eight-membered cobalt-dimer ring (with a Co−Co distance of 3.711 Å) through the acetate side chains on either side, and the cis conformation of the pda^{2-} forms a 22-membered metallocycle by linking these cobalt dimer rings (Figure 4b). The metallocycle acts as a four connector and extends into two dimensions with another four metallocycles through the bridging hydroxyl group (μ_2-OH) with Co−Co distances of 3.476 Å through the crystallographic *bc* plane (Figure 4c). This 2D network is again, in turn, connected by the coligand ptz in a μ_4 coordination mode (μ_3 from the tetrazole ring and μ_1 from the pyridine ring of the ptz). The coligand ptz^{1-} again links the Co dimer ring with the nitrogen donors by linking the N5 atom from the pyridine ring and the N3 atom of the tetrazole ring to Co atoms (which resemble the coordination mode of 4,4′-bipyridine). Because of the availability of more donor sites in the tetrazole moieties, they are known to adopt at least nine distinct types of coordination modes and the geometry of the donor sites allows coordination of the surrounding metal polyhedra at the shortest distances.[24] In the present system, the tetrazole ring coordinates to three Co atoms through the three nitrogen atoms (N1, N2, N4), that is, two Co atoms from the one Co dimer ring and one Co atom from another dimer, thereby forming a 1D chain in which the Co atoms are bridged by tetrazole rings and μ_2-OH groups (Figure 4d). Because of the cis conformation of the pda^{2-} anion, a metallocycle ring has been formed which further extends by the bridging with the μ_2-OH group and tetrazole ring to form 2D layers as shown in Figure 4e.

*$[Co(hfipbb)(bix)_{0.5}]_n$ (**5**).* The asymmetric unit in the crystal structure of compound **5** consists of one cobalt atom, one $hfipbb^{2-}$ ligand, and half of the bix ligand. Compound **5** crystallizes in a monoclinic space group *C*2/*c*. Crystallographic analysis reveals the 2D interpenetrated metal-acid layers which

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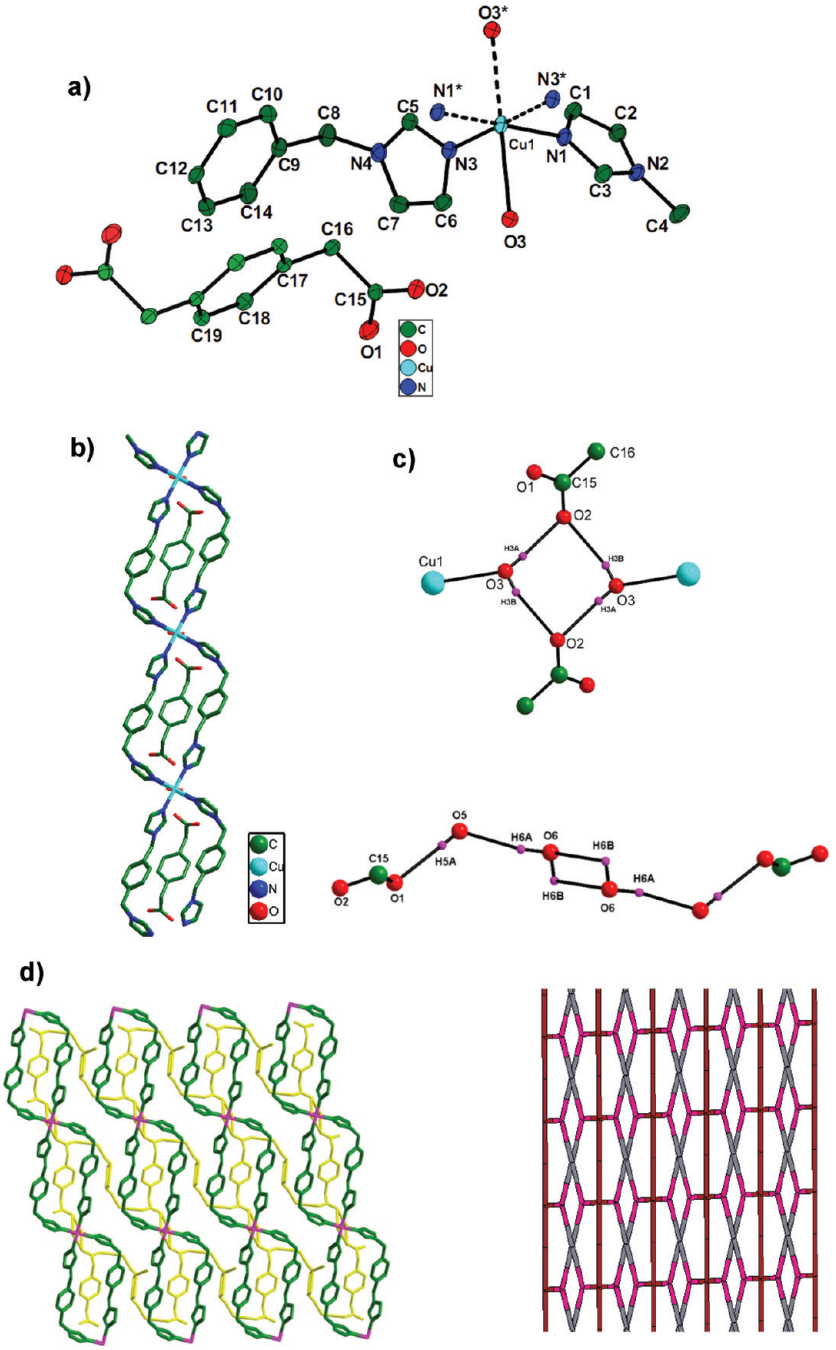

Figure 3. (a) Thermal ellipsoid plot of **3**, (b) 1D double chains constituted by bix ligands incorporating pda^{2-} ligands, (c) hydrogen bonded ring motifs constituted by water molecules and carboxylate oxygens, (d) 3D supramolecular structure formed due to hydrogen bondings and its schematic representation.

are connected by the bix ligand giving rise to a 3D pillared layered framework. The 2D interpenetrated metal acid layers are composed of secondary building units (SBUs) of dimetallic tetracarboxylate paddle-wheel clusters bridged by the $hfipbb^{2-}$ moieties (Figure 5a).[25] As displayed in Figure 5a, the coordination geometry of each cobalt atom in the paddle wheel is in distorted octahedron, the equatorial plane of which comprises four oxygen atoms from carboxylate groups of four $hfipbb^{2-}$ ligands, and the apical coordination sites are filled by one nitrogen atom from the bix ligand with a Co−N distance of 2.044 Å and another Co atom of the paddle wheel. The Co−O bond lengths in the SBUs vary in the range of 2.026−2.092 Å, and the intradimer Co−Co separation is 2.858 Å. The dihedral angle between the bent rings of the $hfipbb^{2-}$ ligand is 81.79°; these bent $hfipbb^{2-}$ moieties link four other neighboring paddle

Table 3. Geometrical Parameters Describing the Conformations of pda^{2-} Ligand in Compounds 1−4 (see also Scheme 2)

C. No.	torsion angle τ (deg) $\tau_3(ijj'i')$	$\tau_1(ijkl)$	$\tau_2(l'k'j'i')$	separation between metal atoms (Å)
1	180.0	90.08	−90.08	12.80
2	105.23	174.63	−70.30	12.03
3	180.0	101.92	−101.92	uncoordinated
4	2.35	100.17	−77.27	8.10

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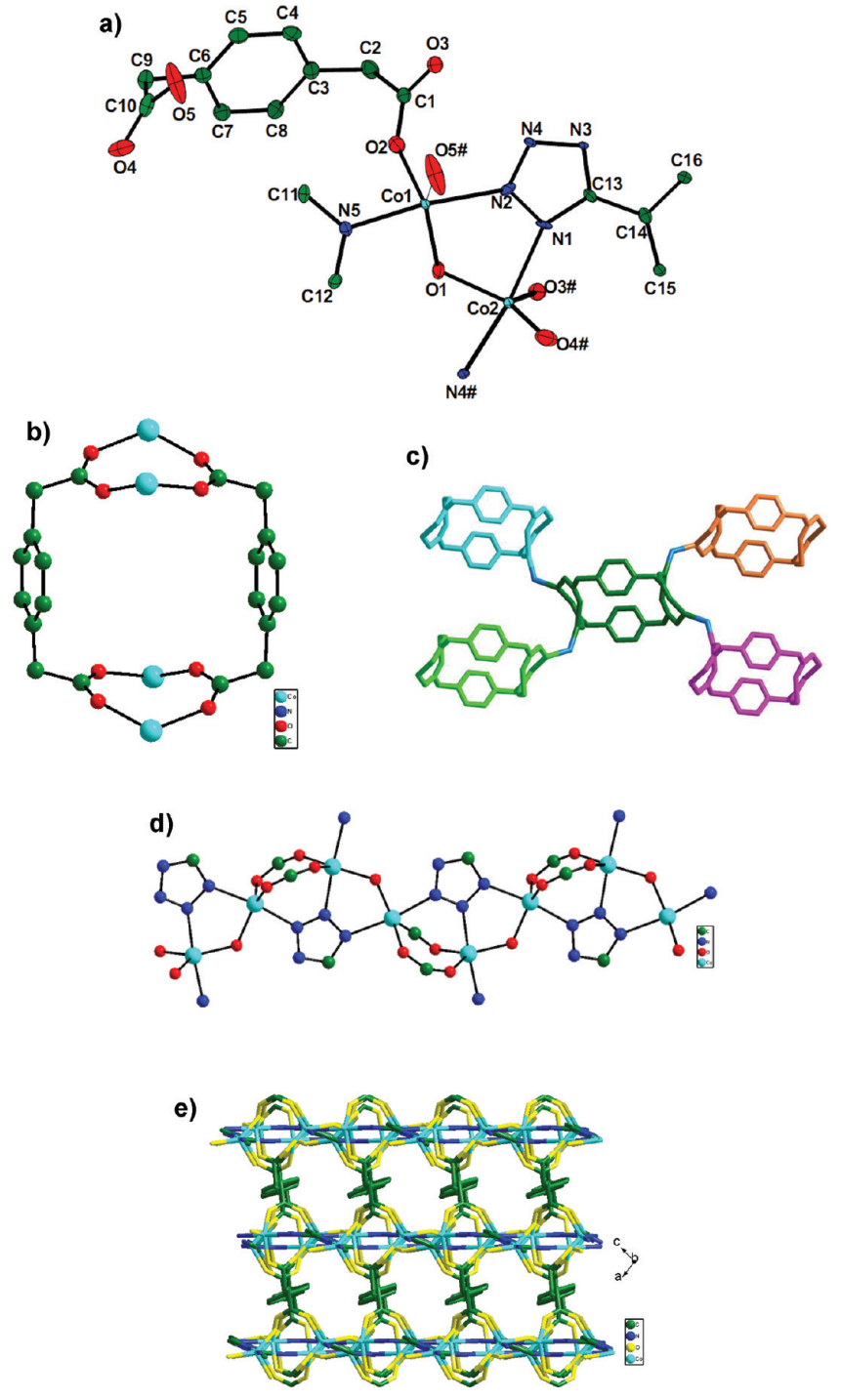

Figure 4. (a) Thermal ellipsoidal plot **4**. (b) Molecular box formed due to cis conformation of the pda^{2-} ligand. (c) Extension of molecular boxes chain through the μ_2-OH group. (d) 1D chain formed chain formed via tetrazole nitrogens, cobalt atoms, and carboxylate oxygen atoms. (e) The overall 2D framework of compound **4**.

wheels resulting in a 2D net with dimensions 14.38 Å × 14.35 Å. The skeleton of these 2D layers can also be viewed as a unique helical tubular double layer, which is similar to the previously reported Co-hfipbb sheets in the compound $[Co(hfipbb)(py)]_n$ (Figure 5b).[25] These helical interpenetrated double layers are extended to a 3D framework with the aid of the flexible exo-bidentate bix ligand. The bix ligand connects the two paddle wheels of two different double layers with a separation of 14.81 Å in a regular trans fashion. The connectivity pattern of linker bix forms 1D chains through the crystallographic *c* axis connecting the double layers in the *ab* plane (Figure 5c). The imidazole rings twist with respect to each other by an antiperiplanar torsion angle of 180° through (N2−C21−C21−N2) indicating trans conformation (Table 4). The two imidazole rings in the bix ligand twist from the phenyl ring plane by a torsion angle of 76.86° through (C18−N2−C20−C21), and the angles between the planes of the imidazole rings and the plane of phenylene group are 67.57° (Table 4). Paddle wheels are considered as six connected nodes and $hfipbb^{2-}$ as linkers to form 2D unique helical double layers, and

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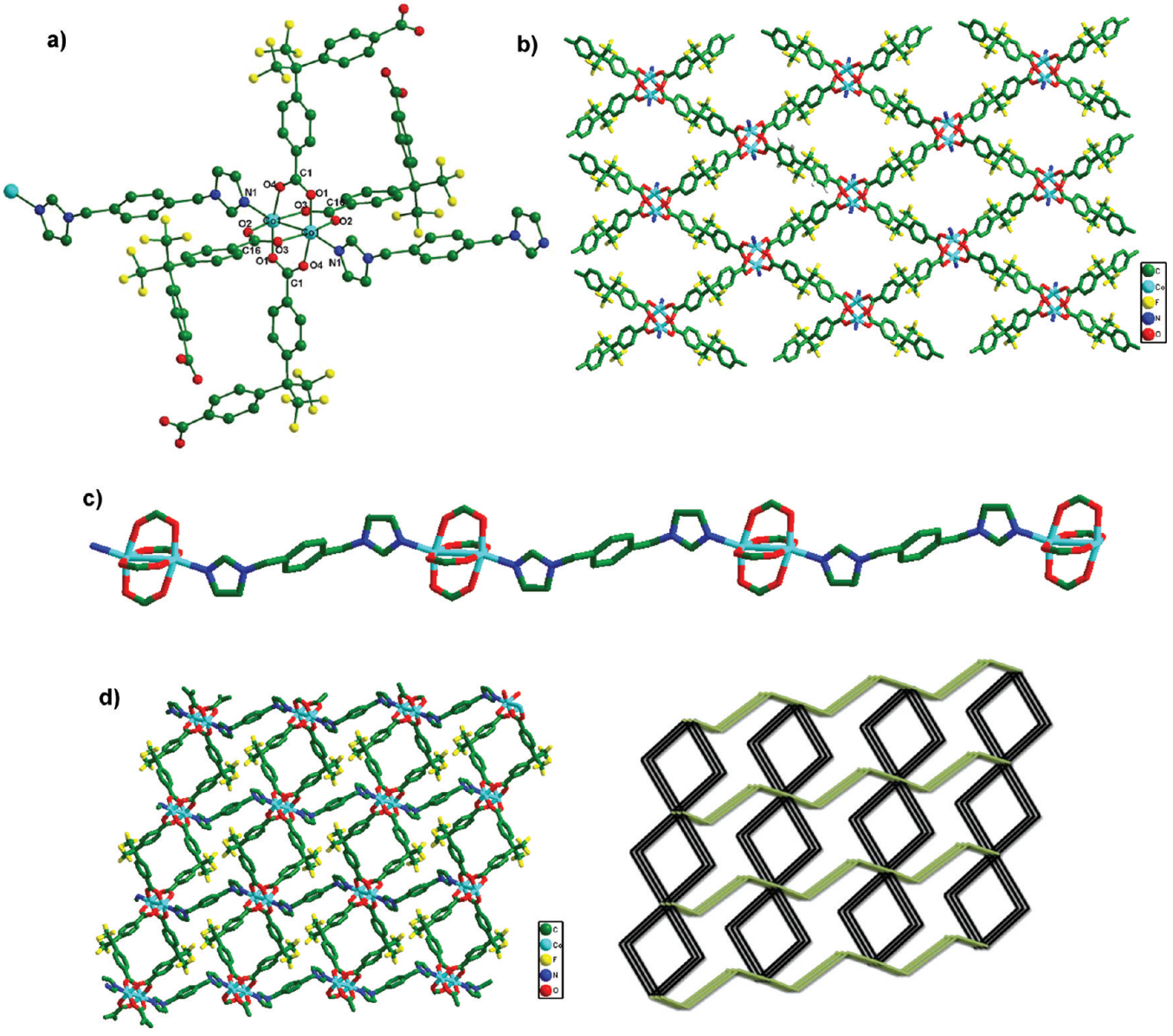

Figure 5. (a) The coordination environment to the Co atoms in the paddle wheel; (b) 2D helical double layer formed via paddle wheels; (c) 1D chain formed by connecting the paddle wheels by the bix ligands; (d) the overall 3D framework of compound **5** and its schematic representation of the 3D framework.

Table 4. Geometrical Parameters Describing the Conformations of bix Ligands in the Compounds 1−3, 5, 6 (See also Scheme 2)

	torsion angle τ (deg)			angle between the aromatic rings (deg)			
C. No.	$\tau_3(jkk'j')$	$\tau_1(ijkl)$	$\tau_2(l'k'j'i')$	X−Y	X−P	P−Y	separation between metal atoms (Å)
1	180.0	51.29	−51.29	0.00	71.62	71.62	15.19
2	77.65	51.02	−102.59	73.05	81.5	82.69	12.03
3	134.58	163.53	−78.75	82.32	80.39	70.89	13.03
5	180.0	76.86	−76.86	0.00	67.57	67.57	14.81
6	A- 180.0	72.76	−72.76	0.00	88.61	88.61	14.02
	B- 174.50	94.73	−105.17	9.36	69.18	73.37	13.96

these layers are pillared by the bix ligand as a linker resulting in the formation of a 3D framework as shown in Figure 5d.

[Co(2,6-pydc)(bix)$_{1.5}$]$_n$·4nH$_2$O (**6**). A single crystal X-ray diffraction study reveals that compound **6** is a 1D ladder-like structure that crystallizes in triclinic space group $P\bar{1}$. As shown in Figure 6a, Co(II) is in distorted octahedral coordination sphere that is defined by the two nitrogen donors from two different bix ligands in apical positions, and two carboxylate oxygens and one nitrogen donor from one 2,6-pydc and one bix nitrogen atom in the basal plane. 2,6-pydc[26] blocks the three coordination sites of the Co(II) octahedron and leaves the three coordination sites for the bix nitrogen atoms. The three bix ligands attached to the Co(II)-octahedron connects to three other cobalt atoms with a separation of 13.96 Å and 14.02 Å to

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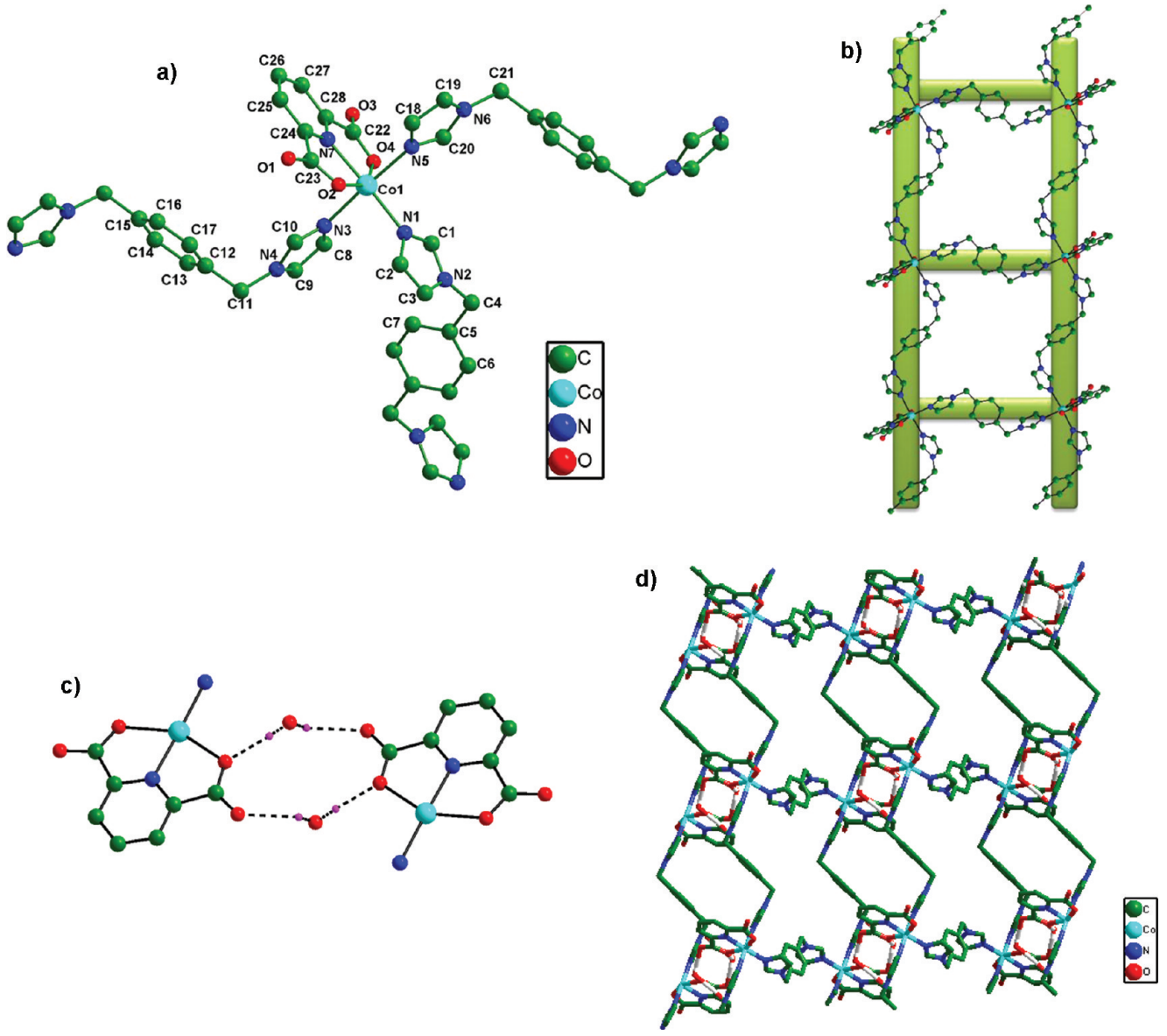

Figure 6. (a) The immediate coordination environment of the Co atom in compound **6**, (b) 1D ladder running though the *a* axis, (c) 12-membered hydrogen bonded ring formed by the assistance of water molecule and carboxylate oxygen atoms, (d) 2D supramolecular network formed due to classical hydrogen bondings.

form a square box with Co(II)-2,6−pydc complex as the corner and bix ligands as edges; it extends to a 1D ladder structure (Figure 6b). Two types of bix ligands are involved in the formation of a 1D ladder based on different conformations. The bix ligand represented by {N3N4N6N5} connects two cobalt atoms with a separation of 14.02 Å, and the bix ligand represented by {N1N2N2N1} creates a separation of 13.96 Å between the two cobalt atoms. The imidazole rings in the bix {N3N4N6N5} twist with respect to each other by an antiperiplanar torsion angle of 174.50° (through N6−C21−C11−N4) and the imidazole rings twist with respect to the phenyl ring by 94.73 (through C12−C11−N4−C9) −105.17° (through C12−C11−N4−C9). In the other bix ligand {N1N2N2N1}, the imidazole rings twist with respect to each other by an antiperiplanar torsion angle of 180° and twist with respect to the phenyl ring by 72.76° (Table 4).The bix ligand does not show any unusual conformation to meet the coordination requirements imposed by the Co(II)-octahedron and is confined to a typical trans conformation of antiperiplanar torsion angles of 174.50° (a slight deviation from the regular trans conformation of 180°) and 180°. As anticipated, classical hydrogen bonding between lattice water molecules and carboxylate oxygens was observed with O···O distances varying from 2.774(5) to 2.935(7) Å, and nonclassical hydrogen bonds were observed between C−H moieties and carboxylate oxygens as well as lattice water molecules (Table 2). With the assistance of the lattice water molecule (O8) and the carboxylate oxygens (O3 and O4), a 12-membered hydrogen bonded ring $R^4_4(12)$ has been formed between the two 1D ladders (Figure 6c). The connectivity pattern of these rings to connect the 1D ladders extends to form a 2D supramolecular network (Figure 6d).

Factors Affecting the Conformations of the Flexible Ligands in the Self-Assembly of the Coordination Networks. The conformational rotations of the flexible ligands H_2pda and bix in all six compounds (**1**−**6**) have been studied under three different schemes to rationalize the effects

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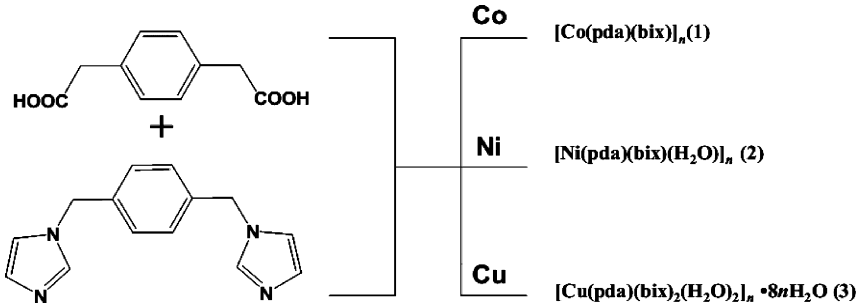
Scheme 3

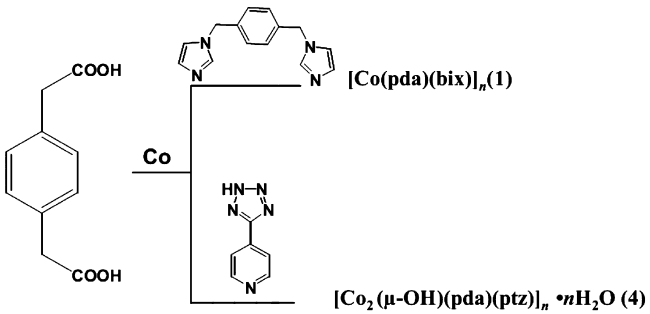


of (i) coordination geometries of different metal ions in modulating the conformations of the flexible ligands, (ii) conformational modulation of the pda^{2-} by increasing the number of donor sites and rigidity in the N-donor coligand, and (iii) geometry of the carboxylate ligands in the conformational changes of the N-donor ligand bix.

As shown in Scheme 3, three structurally different compounds **1**−**3** have been prepared by varying the metal ions. The cobalt atom in compound **1** is present in the distorted tetrahedral environment (two carboxylate oxygens from two pda^{2-} ligands, two nitrogens from bix ligands), and both the flexible ligands pda^{2-} and bix in the structure adopt a regular trans conformation with a predicted antiperiplanar torsion angle of 180° (Table 4) to give a 3D framework, whereas in compound **2** the nickel atom is present in a distorted octahedron (three carboxylate oxygens from two carboxylic acids, two nitrogens from different bix ligands and one aqua ligand) and the two imidazole rings in the bix ligand exhibit a synclinal torsion angle of 77.65°, and the two acetate groups in the pda^{2-} show an anticlinal torsion angle of 105.23° to meet the coordination requirements imposed by the metal ions. In compound **3**, in which the Cu(II) atom is present in a slightly distorted octahedron (four nitrogens from different bix ligands and two aqua ligands) and the two imidazole rings in the bix exhibit an anticlinal torsion angle of 134.50°, the two acetate groups in the pda^{2-} show a typical trans conformation of antiperiplanar torsion angle of 180°. A careful analysis of these three structures reveals that the coordination of aqua ligands (one in **2**, two in 3) to metal polyhedra restricts the coordination sites for the ligands to coordinate to the metal thereby these flexible ligands modulate their conformations in order to meet the coordination geometry at the metal polyhedra. Thus, it can be said that the blocking at the coordination sites of the metal polyhedra allows the regulation of the conformations of the flexible ligand. This approach of blocking the coordination sites has worked out in our previous report[13] to achieve the cis conformation of the *p*-xylylene-diphosphonic acid along with the trans conformation. The bix ligand exists in three conformations with torsion angles antiperiplanar (trans), synclinal (toward cis), anticlinal (toward trans) in compounds **1**, **2**, and **3**, respectively. In a similar fashion pda^{2-} exists in two conformations: antiperiplanar (trans) in compounds **1** and **3**; anticlinal (toward trans) in **2**. From the previous reports,[27] the trans conformations always lead to formation of higher dimensional frameworks and the cis conformations leads to closed rings. In compound **1**, cobalt with coordination number 4 adopts the trans conformation of both ligands to form a 3D framework, whereas the Ni and Cu in compounds **2** and **3** with coordination number 6 adopts the anticlinal and synclinal conformations of the ligands thereby forming 1D extended ring structures. The thermodynamically more stable trans forms dominate in almost all the complexes of the previous reports,[28] and as a result the factors governing the conformational control of these ligands are of particular interest in assembling the coordination networks involving flexible ligands. In view of these factors, compounds **1**−**3** represent a classical example in which the coordination geometry of the metal ions plays an important role in modulating the conformations of the flexible ligands.

The factors that modulate the conformations of the flexible ligand pda^{2-} have been studied by varying the N-donor ligands from flexible bidentate to rigid multidentate ligand (Scheme 4).

Scheme 4



From the previous report[15] in the M(II)−pda^{2-} system, pda^{2-} exists in the trans conformation. In compound **1**, pda^{2-} is confined to typical trans conformation by employing flexible bidentate ligand bix, whereas pda^{2-} adopts a cis conformation with a synperiplanar torsion angle of 2.35° by using a rigid pentadentate ligand 4-ptz. In a dual ligand system, the conformational changes in one of the ligands is strongly influenced by the coordination pattern of the other ligand. By changing the flexible coligand to rigid ligand the thermodynamically favored trans conformation has been changed to cis conformation. This type of rigidity modulated conformation of pda^{2-} has been demonstrated by Cao and co-workers by introducing the rigid 4,4-bipyridine to a metal-carboxylate system.[15] Rigid coligand has more ability to modulate the conformation of the flexible ligand than flexible coligand.

As shown in Scheme 5, in order to study the different conformations of the bix ligand, we have employed three carboxylic acids with different geometrical dispositions of carboxylate group to synthesize the compounds **1**, **5**, and **6**. A flexible carboxylic acid H_2pda, bent carboxylic acid $H_2hfipbb$, and rigid blocking carboxylic acid 2,6-H_2pydc employed impose the same conformations to the bix ligand, in a typical trans conformation in all the three compounds **1**, **5**, and **6**. The three

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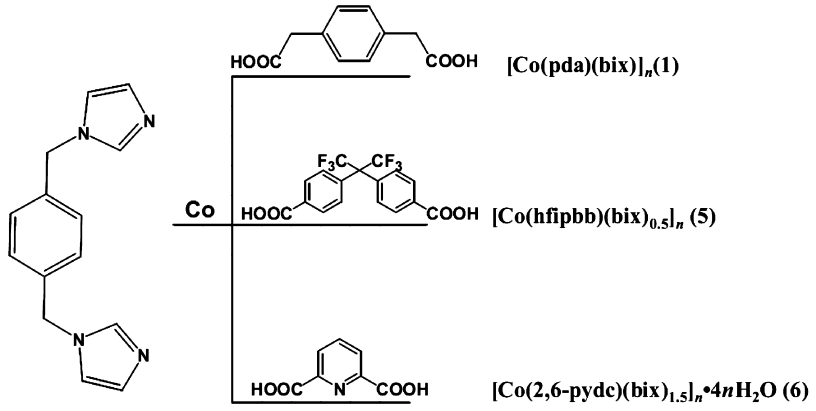
Scheme 5



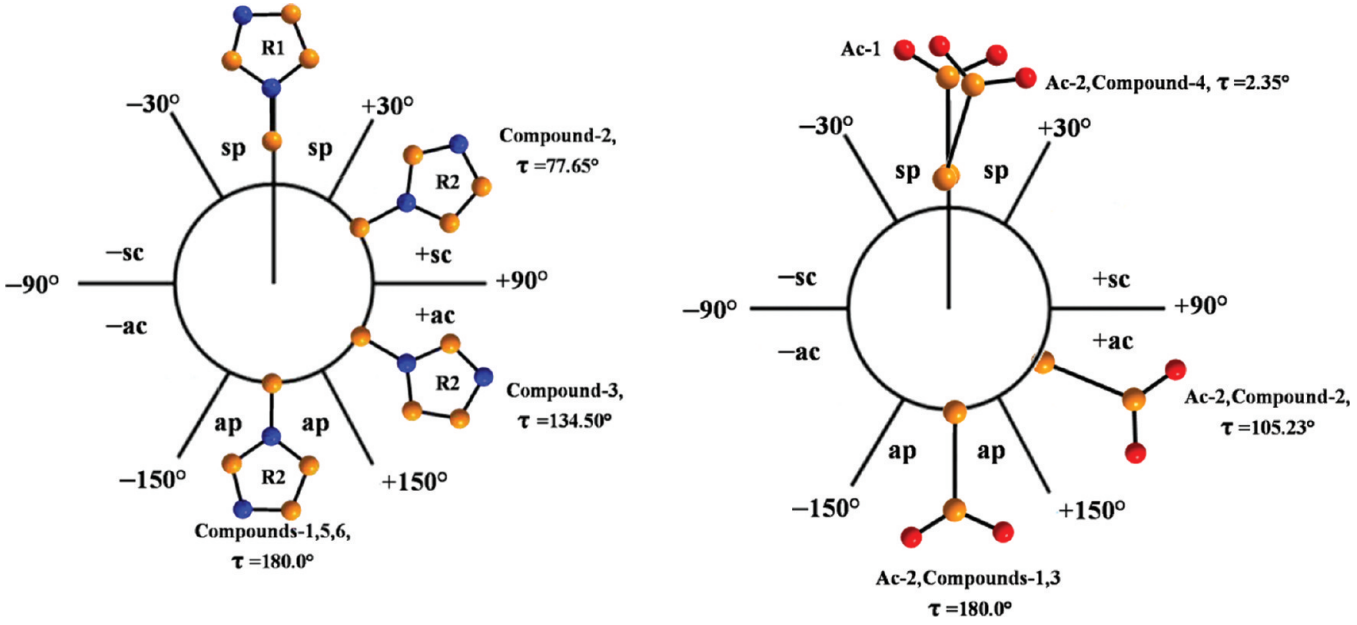


Figure 7. Newmann projection representation of the bix (left) and pda^{2-} (right) ligands; R1 and R2 represent the imidazole rings in the bix ligand. Ac-1 and Ac-2 represent the acetate groups in the pda^{2-} ligands. The angle is measured with respect to each imidazole ring or acetate groups, not with respect to the phenyl ring. So R1 and Ac-1 is taken at the mean position and the orientation of the other rings/groups has been shown.

carboxylic acids used do not modulate the thermodynamically stable trans conformation to other conformations. But the steric requirements imposed by the carboxylate groups on the metal polyhedra allow the bix ligands to twist their imidazole rings with respect to the phenyl group to certain extents, that is, 51.29° in **1**, 76.86° in **5**, and 94.73° in **6** (Table 4). In compound **6**, there is a slight deviation from the trans conformation and it exhibits an antiperiplanar torsion angle of 174.50°. The conformational control of the bix ligand solely depends on the coordination requirements imposed by the metal octahedron, which in turn depends on the steric requirements created by the carboxylate ligands. By changing the geometry of the carboxylate group, the imidazole rings in the bix ligand twist with respect to the phenyl ring to a certain extent maintaining a twist with respect to each other by the same angle. The Newman projection of the bix and pda^{2-} ligands with the observed torsion angles in compounds **1**−**6** is shown in Figure 7. Different conformations of the flexible ligands change the length of the ligand through various extents, which in turn varies the separation between the metal atoms. Usually, the length of the trans conformer is more than the cis and the gauche conformers have intermediate lengths (Figure 8).

Theoretical Calculations. To compare the stability of the bix and pda^{2-} ligands in their different conformations in the title compounds, theoretical calculations have been performed. The molecular geometries of only the ligands were taken from the CIF files, generated during the crystal structure determination of the compounds, and are optimized. Single point energy calculations have been carried out by using B3LYP with 6-311g** basis set. It is a common practice in the field of polymeric metal complexes to compute the energies, using a model structure that very closely resembles the particular moiety to reduce mainly the computational time.[29] In the present study, we have considered only the ligand geometries, that is, bix in the compounds **1**, **2**, **3**, **5**, and **6**, and pda^{2-} in **1**, **2**, **3**, and **4** without considering coordination for the computational simplification as model structures. These considerations are adopted in these calculations only to compare the energies of the particular conformations in the title compounds. It has been shown, however, that these considerations can have a significant consequence on the absolute values, and therefore,

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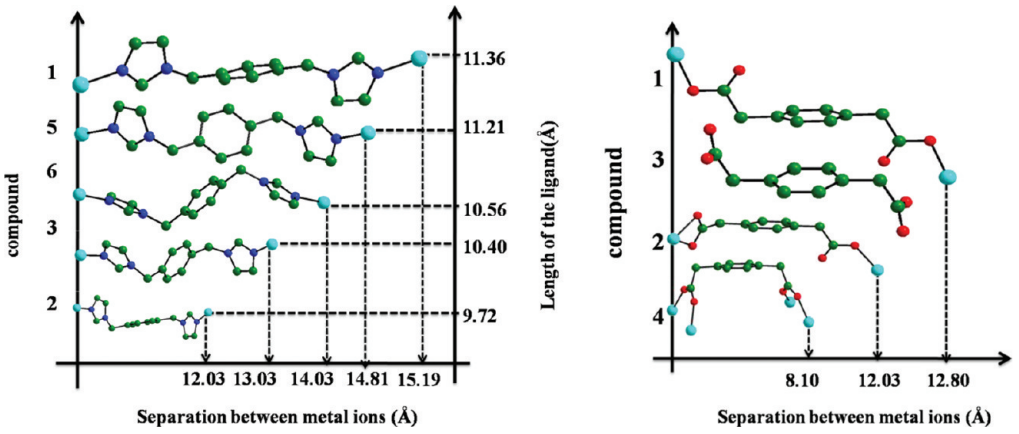

Figure 8. Projections of the bix (left) and pda^{2-} (right) ligands on the scale viewing the length of the ligands and separation created between the metal atoms.

only a qualitative comparison could be expected. From the literature, the energy calculations of the crystal structures have been performed by optimizing the crystal structures through various optimization procedures (Dreiding force field) using density functional theory (DFT) methods.[30]

The optimized energy of the bix ligand in all the compounds show almost the same energy (kcal/mol) in all its conformers, −477592.9776 (−477426.575) for **1**, −477592.8070 (−477427.367) for **2**, −477592.9776 (−477423.600) for **3**, −477592.9887 (−477426.574) for **5**, −477592.7359 (−477421.693) for **6**. The optimized energy of pda^{2-} ligand in all the compounds also show almost the same energy (kcal/mol) in all its conformers −431100.09311 (−431003.7712) for **1**, −431099.4490 (−431004.0174) for **2**, −431100.0836 (−431008.4104) for **3**, −431099.4490 (−431014.2817) for **4**. The values in the parentheses indicate single point energies. From the optimized energy values, all the conformations of the bix ligand converge to global minima in the potential energy surface (which corresponds to energies of stable conformations). This is the case also for the pda^{2-} ligand. A qualitative comparison of single point energy calculations reveals a slight difference in the energy values of the conformers. These results indicate that the bix and pda^{2-} ligands can show stable cis, trans, and gauche conformations, and the energy difference between these conformations are very less, so that the ligand can exist in different conformations depending upon the coordination requirements (see Supporting Information for coordination details and other computational details).

XRPD and Thermogravimetric Analysis (TGA). To ensure the phase purity of the products X-ray powder diffraction data for all the compounds were recorded. Similar diffraction patterns for the simulated data (calculated from single crystal data) and observed data prove the bulk homogeneity of the crystalline solids (see Supporting Information for the PXRD patterns of the compounds **1**−**6**). Although the experimental patterns have a few unindexed diffraction peaks and some are slightly broadened and shifted in comparison to those simulated from the single-crystal data, it can still be regarded that the bulk as-synthesized materials represent compounds. From the TGA curves, the weight of compounds **2**, **3**, and **6** are lost in the beginning due to the losses of solvated water molecules. The slight inconsistencies in the patterns are due to the loosely bonded solvent molecules in the crystal structures.

TGA curves are made under flowing N_2 for crystalline samples **1**−**6** in the temperature range 30−1000 °C (Figure 9).

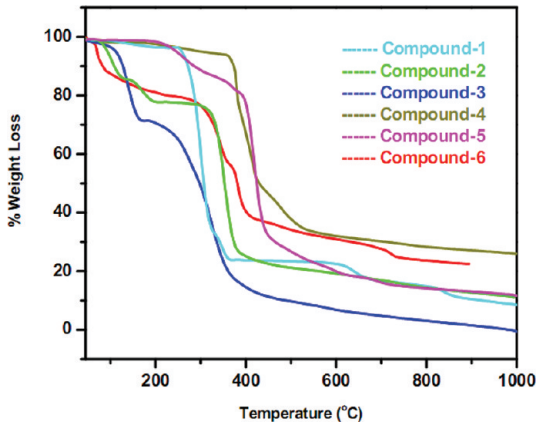

Figure 9. Thermogravimetric curves of compounds **1**−**6**.

Compound **1** exhibits a thermal stability up to 254 °C and undergoes continued weight loss attributed to the decomposition of bix and pda^{2-} ligands. Compounds **2** and **3** show continuous weight losses of the lattice and coordinated aqua ligands followed by the decomposition of organic parts. For compound **4**, a continuous weight loss of 7.78% (calcd, 7.15%) in the region 40−360 °C corresponds to complete loss of lattice water molecule and −OH group and then the framework begins to collapse. Compound **5** exhibits a thermal stability up to 220 °C and then the framework collapses in two steps. Compound **6** shows a weight loss of 11.65% (calcd, 11.02%) in the region 65−122 °C corresponding to the loss of four lattice water molecules. Among all compounds, **4** exhibits a high thermal stability up to 360 °C in which pda^{2-} exists in cis conformation. The thermal stability of the compound constructed by the cis pda^{2-} (which is thermally less stable) is more stable than the compound constructed by the trans pda^{2-} (which is thermally more stable) due to the presence of a rigid multidentate coligand in **4** and flexible bidentate coligand in **1**. The remaining compounds containing bix ligands with trans conformation show higher thermal stability than compounds containing bix ligands with other conformations.

Electronic Properties. Solid state diffuse reflectance (electronic absorption) spectra for compounds **1**−**6** are presented in Section 2 of Supporting Information. The absorption

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peaks at 576, 332, 270 nm (compound **1**), 332, 264 nm (compound **2**), 584, 260 nm (compound **3**), 576, 278 nm (compound **4**), 572, 274, 236 nm (compound **5**), and 520, 344, 270 nm (compound **6**) are observed in the respective spectra. In all the spectra, the lowest energy bands are assigned due to d−d transitions of metal ions Co(II) (**1**, **4**, **5**, and **6**) and Cu(II) (**3**) present in the title compounds, and the highest energy bands are due to Π−Π* and n−Π* transitions from phenyl group and imidazolyl moieties. The conformational changes of the flexible ligands do not affect the absorption peaks in the compounds.

Magnetic Properties. Temperature-dependent magnetic susceptibility χ_m of **4** was measured in an applied *dc* field of 1 kOe in the temperature range 2−300 K (Figure 3a, section 2 in Supporting Information). The $\chi_m T$ value at room temperature is 4.45 cm^3 K mol^{-1} per Co(II) ion, which is much higher than the calculated spin-only value (1.87 cm^3 K mol^{-1}) for an uncoupled high-spin Co(II) ion ($S = 3/2$, $g = 2$) with octahedral geometry, indicating the orbital contribution of Co(II) ions.[31] Upon cooling the $\chi_m T$ value decreases smoothly to reach a value of 1.070 cm^3 K mol^{-1} at 22 K and slightly shifts the curve and then decreases to a minimum value of 0.220 cm^3 K mol^{-1} at 2 K. The presence of a round peak at 6 K in the χ_m vs T indicates a low dimensional antiferromagnetic ordering. The Neel temperature $T_N = 6$ K was determined from the sharp peak in $d\chi_m T/dt$.[32] Because of paramagnetic impurities, the χ_m value increases below 4K. The results show that the compound shows overall antiferromagnetic interactions and also spin−orbit coupling interactions between the adjacent Co(II) ions.

The magnetic susceptibility of compound **5** was measured in an applied *dc* field of 1 T in the temperature range of 2−300 K (Figure 3b, section 2 in Supporting Information). Compound **5** is essentially a Co-dimer with four carboxyl ligands coordinating to two Co(II) ions that form a typical paddle wheel SBU, which is further connected through the axial site by the bix ligand. The $\chi_m T$ value at the room temperature is 6.79 cm^3 K mol^{-1}, which is much higher than the calculated spin-only value of 3.87 cm^3 K mol^{-1} for two Co(II) ion ($S = 3/2$), with octahedral geometry. This indicates the orbital contribution of Co(II) ions to the observed $\chi_m T$ value. The curve indicates the typical antiferromagnetic and spin−orbit coupling interactions present in the compound.

CONCLUSION

In summary, we report here six new coordination polymers (**1**−**6**), based on flexible ligands (H_2pda, bix) by employing the different coligands (4-ptz, H_2hfipbb, 2,6-H_2pydc) to rationalize the factors that modulate the conformational changes of the flexible ligands. Compounds **1**−**3** represent the example in which the coordination geometry of the metal ion plays an important role in modulating different conformations, such as trans, cis, and gauche forms of the pda^{2-} and bix ligands. The availability of the coordination sites around the metal polyhedra is responsible to regulate the degree of flexibility to adopt various conformations to maximize the intra- and intermolecular forces in the crystal structure. Compound **4** represents an example in which the cis conformation of the pda^{2-} ligand is stabilized by the rigid pentadentate ligand 4-ptz. Conformational modulation of the flexible acid ligand under the influence of the rigid and flexible coligands has been studied, and the rigid coligand is preferred as the best selection in achieving the modulation. The effect of the dicarboxylate ligands with different geometrical dispositions of carboxylate groups on the conformations of the neutral flexible coligand bix has been demonstrated. The variations in the deviations of the imidazole rings with respect to the phenyl rings in the bix ligand have been observed by employing these different carboxylic acids. In the self-assembly process of dual ligand containing coordination polymers, the geometry of one of the ligands (such as flexibility, geometry of the coordinating atoms, etc.) transmits to the metal polyhedra and the metal polyhedra influences the geometry in the other ligand and so on. The compounds, reported in this article, represent classic examples to study new perspectives in the mechanism of self-assembly of coordination polymers. Many more systematic studies are needed to rationalize the factors discussed in affecting the conformational modulation of the flexible ligands. Theoretical studies confirm that the stability of the ligands is not altered by adopting different conformations. We have also described thermal, electronic, and magnetic properties of the title compounds.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, IR-, electronic spectra, magnetic susceptibility plots, additional figures, computational outputs and selected bond distances and angles in PDF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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