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Solvent-Dependent Coordination Polymers: Cobalt Complexes of 3,5-Dinitrobenzoic Acid and 3,5-Dinitro-4-methylbenzoic Acid with 4,4′-Bipyrdine

V. R. Pedireddi* and Sunil Varughese

Division of Organic Chemistry, National Chemical Laboratory, Dr. Homi Bhabha Road,
Pune 411 008, India

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The synthesis, structure elucidation, and analysis of the self-assembly of Co(II) complexes of 3,5-dinitrobenzoic acid and 3,5-dinitro-4-methylbenzoic acid with 4,4′-bipyridine have been reported. Formation of the complexes and the self-assembly in the three-dimensional structures have been found to be dependent on the solvents (such as acetone, dimethly sulfoxide, etc.) employed for the synthesis of the aggregates. 3,5-Dinitrobenzoic acid forms two coordination polymers, **1a** and **1b**, from methanol and a mixture of methanol and acetone solvents, respectively, with entirely different recognition patterns. Similarly, 3,5-dinitro-4-methylbenzoic acid also forms two coordination complexes, **2a** and **2b**, incorporating the solvent of the reaction medium into the crystal lattice. Complex **2a** forms a solvated channel structure, whereas **2b** gives a bilayered structure, with the layers being separated by solvent of crystallization (dimethyl sulfoxide) molecules. All the complexes have been characterized by single-crystal X-ray diffraction studies. Complexes **1b**, **2a**, and **2b** crystallize in a monoclinic lattice, but **1a** adopts a tetragonal lattice. The unit cell dimensions are, for **1a**, $a = 8.095(1)$ Å, $b = 8.095(1)$ Å, $c = 46.283\ (6)$ Å, $\alpha = 90°$, $\beta = 90°$, and $\gamma = 90°$ (space group $P4_32_12$, $Z = 4$), for **1b**, $a = 22.774(2)$ Å, $b = 11.375\ (1)$ Å, $c = 22.533(2)$ Å, $\alpha = 90°$, $\beta = 104.15(1)°$, and $\gamma = 90°$ (space group $P2_1/c$, $Z = 4$), for **2a**, $a = 17.657(6)$ Å, $b = 18.709(4)$ Å, $c = 21.044(6)$ Å, $\alpha = 90°$, $\beta = 108.68(3)°$, and $\gamma = 90°$ (space group, $C2/c$, $Z = 8$), and, for **2b**, $a = 11.025(5)$ Å, $b = 15.139(4)$ Å, $c = 11.443(4)$ Å, $\alpha = 90°$, $\beta = 97.48(3)°$, and $\gamma = 90°$ (space group $P2/n$, $Z = 2$). In all the complexes **1a**, **1b**, **2a**, and **2b**, the basic interaction between Co(II) and 4,4′-bipyridine remains the same with the formation of linear Co–N dative bonds, but the carboxylates display various modes of interaction with Co(II). The average Co–N and Co–O distances are 2.161 and 2.108 Å, respectively.

Introduction

The design and synthesis of coordination compounds dates back to the pioneering work of Cotton and others carried out in the last few decades, in which emphasis was focused on the creation of molecular entities to meet the requirements of tailor-made applications such as catalytic activity, performance of selective chemical reactions, etc., exactly the manner in which conventional organic synthesis is being carried out to synthesize targeted compounds.[1,2] However, the successful creation of supramolecular assemblies through noncovalent bonds such as hydrogen bonds[3−5] employing organic entities directed the utilization of highly directional coordinate bonds also to create functionalized solids in the form of organic−inorganic hybrids[6−8] with intriguing structural motifs and potential applications.[9,10] The main advantage of these systems is the formation of rigid networks through strong coordinated bonds unlike the counterparts of purely

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* Author to whom correspondence should be addressed. E-mail: pedireddi@ems.ncl.res.in.

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organic based systems, which are being created by weak bonds such as hydrogen bonds. We find numerous examples of hybrid structures in the literature,[11] the majority of which were created by employing organic compounds with functional groups having affinity toward metal ions placed at the required positions to give desired architectures. In this respect, a vast majority of studies are being carried out using the carboxylate group, and indeed, hybrid structures formed between trimesic acid and Co(II), reported by Yaghi and coworkers, could be regarded as representative examples for the implication of dative bonds in supramolecular chemistry.[12] Also, splendid contributions from several groups of researchers such as Zaworotko,[13] Braga,[14] Hosseini,[15] Stang,[16] etc., employing different types of ligands with multiple bridging moieties (in particular, 4,4′-bipyridyl), are quite noteworthy. Nevertheless, the studies are more often focused on using organic ligands having functional groups that are exclusively able to form dative bonds such that porous structures could be synthesized which find applications in catalysis and molecular adsorption.[9,10] However, instead, organic ligands with noncoordinated functional groups such as $-NO_2$, $-NH_2$, etc. in conjunction with carboxylate groups are considered for the creation of supramolecular assemblies. A variety of novel materials would result, due to the simultaneous formation of dative bonds and noncovalent bonds, because these functional groups are well-known to form robust and strong hydrogen bonds, but such studies are limited. In this direction, we are interested to utilize the knowledge of dative bonds as well as noncovalent bonds (for instance, hydrogen bonds of different strengths such as $O-H\cdots O$, $C-H\cdots O$, etc.) to create novel coordination complexes that can yield different networks such as polymers, channels, layers, etc. in their three-dimensional structures. Since tuning of hydrogen bonds can be done with a change of the solvent system of the reaction medium,[17] one could obtain different architectures at ease by carrying out a reaction in different solvents. As a result, either polymorphs or pseudopolymorphs can be obtained easily utilizing both

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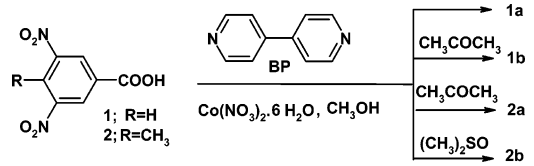
dative bonds and noncovalent bonds.[18] To evaluate some of these features of coordination complexes, we have considered 3,5-dinitrobenzoic acid, **1**, and its 4-methyl-substituted derivative (toluic acid), **2**, to form complexes with cobalt nitrate, and the results are described in the following sections. The choice of these acids lies with the fact that numerous organic assemblies of both acids **1** and **2** are well-known in the literature,[19] but only a few metal complex studies are reported.[20] Further, in this process, 4,4′-bipyridine (bpy) has been chosen as a coligand,[21] because it is well-known for its robustness to act as a spacer to enhance the intermetal distance, which may facilitate the coordination between the metal ion and bulky organic molecules such as **1** and **2** due to the minimization of crowding. In addition, bpy also has the ability to form hydrogen bonds such as C−H⋯O through its acidic phenyl hydrogens with the $-NO_2$ groups of acids **1** and **2**.[22]

Results and Discussion

Cocrystallization of 3,5-dinitrobenzoic acid, **1**, or the corresponding toluic acid, **2**, with 4,4′-bipyridine and cobalt nitrate gave different types of coordination polymers with variation of the solvent of crystallization. Thus, complexes **1a**, **1b**, **2a**, and **2b** were obtained as listed in Scheme 1. The reactions were carried out at ambient conditions, simply by heating the reaction mixtures in a water bath to dissolve the reactants. Nevertheless, the colossal differences in the obtained products are quite intriguing.

Scheme 1



In complexes **1a** and **2a**, the solvent of crystallization (CH_3OH) is coordinated to the metal ion. However, in **1b** and **2b**, the solvent molecules, acetone and dimethyl sulfoxide (DMSO), respectively, are being incorporated into the crystal lattices as guest molecules. The salient feature of all four complexes will be discussed in this paper, highlighting similarities and differences, independently and collectively, so that a wide range of new assemblies can be synthesized employing derivatives of dinitrobenzoic acid in conjunction with metal salts.

Complexes $[Co(C_7H_3N_2O_6)_2(C_{10}H_8N_2)_2(CH_3O)_2]$, 1a, and $[Co_4(C_7H_3N_2O_6)_8(C_{10}H_8N_2)_8(CH_3O)_2]CH_3COCH_3$, 1b. 1 forms a 2:1:1 complex, which we label **1a**, with 4,4′-bipyridine (bpy) and cobalt nitrate, respectively, upon dissolving the constituents in a methanol solution and subsequent slow evaporation over a period of 2 days at ambient conditions. The crystal structure determination reveals that complex **1a** crystallizes in a noncentrosymmetric space group, $P4_32_12$. Complete details of the crystallographic information are given in Table 1.

In the asymmetric unit, both acid **1** (in its carboxylate form) and bpy interact with Co(II), forming Co−O and Co−N dative bonds, respectively. Selected bonding parameters of carboxylate **1** and bpy are given in Tables 2 and 3, respectively. The molecular arrangement around Co(II) is shown in Figure 1a. Thus, each Co(II) is connected to two bpy molecules and two carboxylate molecules of **1** and completes the 6-fold coordination with the aid of two CH_3OH molecules to yield an octahedral arrangement. The two nitrogen heteroatoms on bpy form two distinct Co−N distances, 2.170 and 2.187 Å. All the metal−ligand distances are listed in Table 2. The carboxylate of **1** interacts with Co(II), in a monodentate fashion, with a Co−O distance of 2.070 Å (Table 2), and the uncoordinated oxygen atom forms weak intermolecular C−H⋯O hydrogen bonds. A schematic representation of the Co−O bonding pattern is shown in Chart 1a. The observed pattern, indeed, is topologically identical to that of the catemeric hydrogen bonding[23] between carboxylic acid groups in organic crystal structures (Chart 1a).

Thus, in a typical octahedron, while bpy molecules lie at the axial positions, carboxylates and methanol molecules

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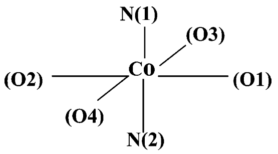
Table 1. Crystal Data, Structure Determination, and Refinement Parameters of Coordination Complexes **1a**, **1b**, **2a**, and **2b**

	1a	**1b**	**2a**	**2b**
chemcial formula	$(C_7H_3N_2O_6)_2(C_{10}H_8N_2)Co^{II}$-$(CH_3O)_2$	$(C_7H_3N_2O_6)_4(C_{10}H_8N_2)_2Co^{II}_2$-$(CH_3O)(C_3H_6O)$	$(C_8H_5N_20_6)_2(C_{10}H_8N_2)Co^{II}$	$(C_8H_5N_2O_6)_2(C_{10}H_8N_2)Co^{II}$-$(H_2O)_2(C_2H_6SO)_2$
fw	699.41	1363.80	665.39	841.55
cryst habit	needlelike	needlelike	needlelike	needlelike
cryst color	pale pink	pale pink	pale pink	pale pink
cryst system	tetragonal	monoclinic	monoclinic	monoclinic
space group	$P4_32_12$	$P2_1/c$	$C2/c$	$P2/n$
a (Å)	8.095(1)	22.774(2)	17.675(6)	11.025(5)
b (Å)	8.095(1)	11.375(1)	18.709(4)	15.139(4)
c (Å)	46.283(6)	22.533(2)	21.044(6)	11.443(4)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	90.00	104.15(1)	108.68(3)	97.48(3)
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	3033 (7)	5660.2(9)	6592(3)	1893.8(12)
Z	4	4	8	2
D_{calcd} (g cm^{-3})	1.532	1.600	1.341	1.476
T (K)	293	293	293	293
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	0.646	0.687	0.586	0.641
2θ range (deg)	46.52	46.60	46.36	46.60
limiting indices	$-8 \le h \le +7$ $-8 \le k \le +6$ $-51 \le l \le +51$	$-25 \le h \le +23$ $-12 \le k \le +12$ $-25 \le l \le +24$	$-19 \le h \le +1$ $-20 \le k \le +18$ $-10 \le l \le +21$	$-12 \le h \le +12$ $-16 \le k \le +16$ $-6 \le l \le +12$
F(000)	1428	2780	2712	854
no. of reflns measd	12826	23238	5005	7728
no. of unique reflns	2169	8158	3085	2726
no. of reflns used	1957	3933	2318	1972
no. of params	250	830	420	262
GOF on F^2	1.229	1.121	1.338	1.061
R1 [$I > 2\sigma(I)$]	0.050	0.104	0.099	0.052
WR2	0.114	0.215	0.282	0.140
final diff Fourier map (e$^-$·Å^{-3}), max, min	0.270, −0.536	0.748, −0.812	1.251, −0.623	0.644, −0.403

Table 2. Details of the Coordinate Bond in the Complexes **1a**, **1b**, **2a**, and **2b**



bond	1a	1b[a]	1b[b]	2a	2b
Co−N(1)	2.170	2.153	2.140	2.156	2.175
Co−N(2)	2.187	2.143	2.153	2.157	2.174
Co−O(1)	2.070	2.053	2.087	2.041	2.080
Co−O(2)	2.070	2.040	2.094	2.068	2.080
Co−O(3)	2.139[c]	2.103	2.106	2.217[d]	2.139[e]
Co−O(4)	2.139[c]	2.162[c]	2.119[c]	2.218[d]	2.139[e]

[a] Terminal metal. [b] Middle metal center. [c] Bonds from MeO. [d] Chelated bonds. [e] Bonds from H_2O.

occupy the equatorial sites. A noteworthy feature is that the phenyl moieties of **1** and methyl groups of CH_3OH lie above and below the basal plane constituted by Co(II) and Co−O bonds, and further, either the two carboxylates or the two CH_3OH molecules are situated at *trans* positions to each other with respect to Co(II); see Figure 1a. Further, coordination complex **1a** forms infinite linear polymer chains, joining the adjacent octahedrons through bpy molecules. In three-dimensional arrangement, these polymer chains are arranged in a crossed manner and interact with each other through weak C−H···O hydrogen bonds. The arrangement of these polymer chains, in a truncated form, is shown in Figure 1b. It is evident that the weak C−H···O hydrogen bonds are formed between the $-NO_2$ group and hydrogen atoms of the bpy and methanol molecules. The H···O distances involving bpy are 2.85 and 2.90 Å, whereas the similar distance formed by CH_3OH molecules is 2.73 Å (Table 3).

However, **1** forms an entirely different type of coordination polymer with cobalt nitrate and bpy upon crystallization from a methanol/acetone mixture. The crystal structure determination (see Table 1) reveals the presence of the solvent of

Table 3. Characteristics of C−H···O Hydrogen Bonds[a] Observed in Complexes **1a**, **1b**, **2a**, and **2b**

1a			**1b**			**2a**			**2b**		
2.73	3.73	139.2	2.52	3.45	173.1	2.90	3.80	164.9	2.72	3.32	123.7
2.85	3.36	126.8	2.60	3.51	167.9	2.44	3.20	136.9	2.68	3.59	166.7
2.90	3.51	126.1	2.84	3.76	161.0	2.95	3.67	134.7			
			2.84	3.73	159.9	2.66	3.26	120.9			
			2.86	3.75	158.8						
			2.49	3.34	152.8						
			2.93	3.78	152.8						
			2.67	3.52	152.5						
			2.75	3.56	145.3						
			2.89	3.65	140.0						

[a] Three columns for each complex represent the distances H···O and C···O (Å) and the angle C−H···O (deg), respectively.

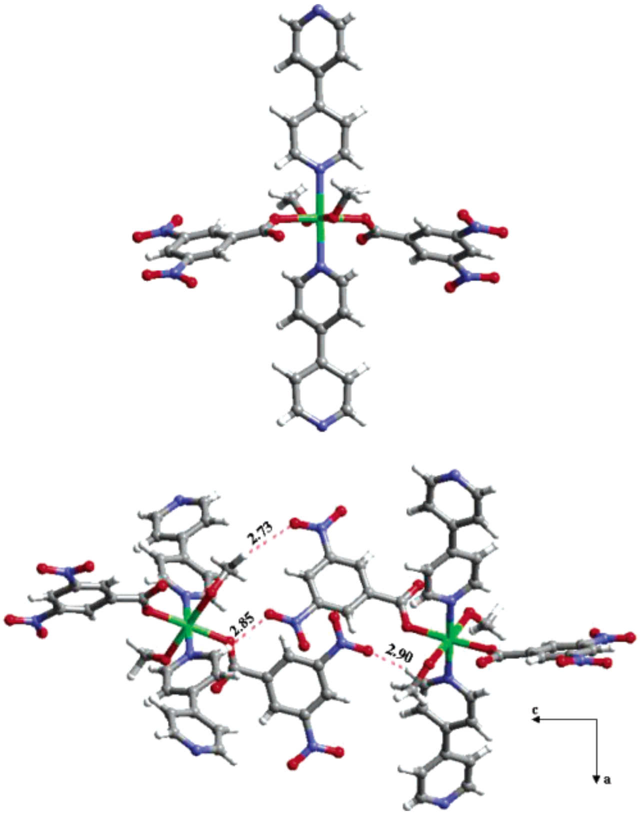
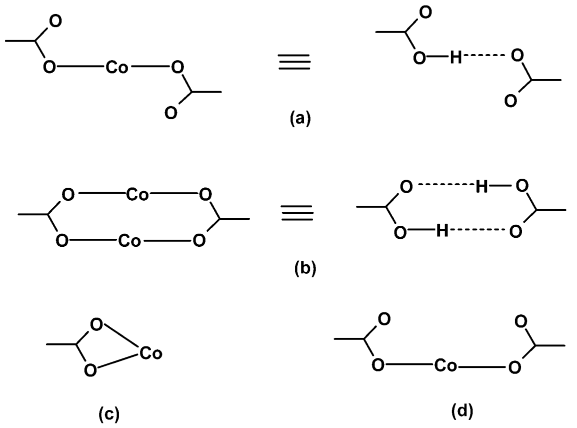


Figure 1. (a, top) Coordination polymer unit observed in complex **1a**. (b, bottom) Interaction between the perpendicular polymer units through C−H···O hydrogen bonds. Dashed lines represent the hydrogen bonds. Color coding: green, Co(II); red, O; blue, N; gray, C; white, H.

Chart 1



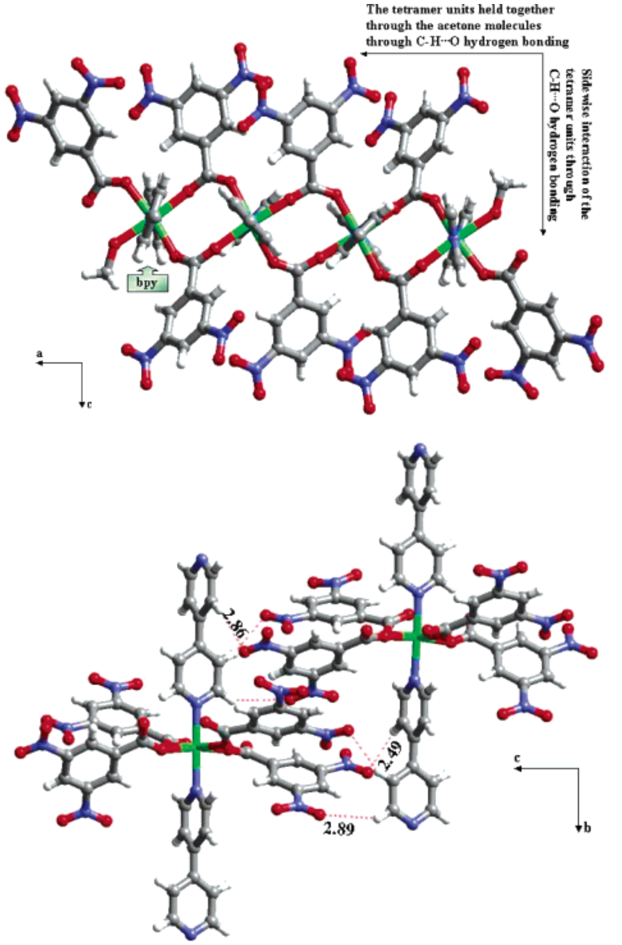


Figure 2. (a, top) Representation of the tetrameric polymer unit in the crystal structure of **1b**, viewed along [010]. (b, bottom) Interaction between the adjacent polymer blocks. Dashed lines represent C−H···O hydrogen bonds.

crystallization, acetone, in the crystal lattice. The constituents (excluding the solvent of crystallization) have a composition of 4:2:2, which is different from that of **1a**. A molecular unit of the coordination complex is shown in Figure 2a.

Analysis of the molecular arrangement discloses a unique pattern with four Co(II) atoms, eight molecules of **1** and bpy each, and two molecules of methanol in every tetrameric unit. In a typical unit, all Co(II) atoms are attached to carboxylate **1** and bpy through Co−O and Co−N coordinate bonds, respectively. As in **1a**, all the Co−N bonds are identical with an average distance of 2.147 Å. However, unlike in **1a**, the carboxylate group in complex **1b** has two different modes of interaction with Co(II), forming a single Co−O bond (in a monodentate fashion) with terminal Co(II), but two Co−O bonds (as a bridged bidentate ligand) with the two intermediate Co(II) ions. Further, two terminal Co(II) ions have coordinated methanol molecules also, along with carboxylates and bpy, to fulfill the 6-fold coordination. As a result, although octahedral geometry is found around each Co(II), the ligands around the terminal Co(II) are different from the intermediate ones.

Thus, in the octahedral arrangement, around each Co(II), molecules of bpy are situated at axial positions, but depending upon the placement of Co(II) (terminal or middle), either carboxylates alone or carboxylate and methanol together form the basal plane. These quadrate cobalt-centered units constitute a three-dimensional arrangement in such a manner that the adjacent units form a polymer block-type structure by joining the adjacent tetramers through Co−N bonds along [010]. Packing of these blocks is shown in Figures 2b and 3. It is evident that, along a lateral direction, the blocks are held together by C−H···O hydrogen bonds formed between the $-NO_2$ groups of **1** and phenyl hydrogens of bpy (Figure 2b). The H···O distances are in the range 2.49−2.89 Å. However, acetone (solvent of crystallization) molecules are inserted as guest species between the adjacent blocks (Figure 3), along the Co(II)−bpy bonding direction. Further, acetone molecules interact with the cages by establishing C−H···O hydrogen bonds formed between the methyl groups of

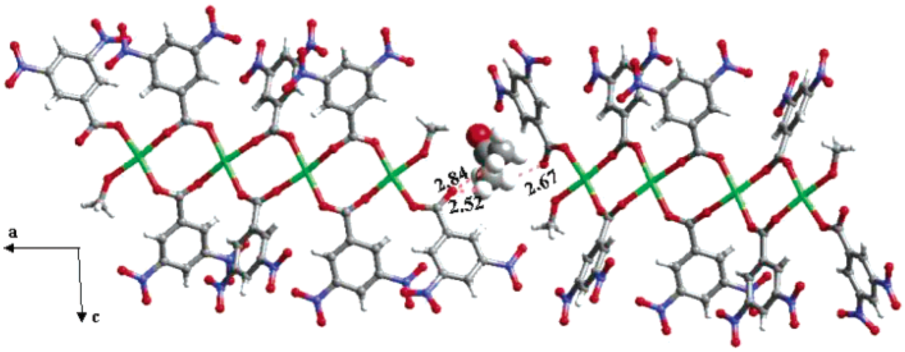


Figure 3. Placement and interaction of acetone molecules between the coordination polymer units.

acetone and the uncoordinated oxygen atom of a terminal carboxylate. The H···O distances are in the range 2.52−2.87 Å.

Complex $[Co_2(\mu^2\text{-}C_8H_5N_2O_6)_2(\mu^2\text{-}C_8H_5N_2O_6)_2(C_{10}H_8N_2)4]$, 2a. 2 forms a 2:1:1 complex, **2a**, with cobalt nitrate and 4,4′-bipyridine upon crystallization from a methanol solution. The stoichiometry was determined from the structure determination by single-crystal X-ray diffraction methods. As was observed in **1a** and **1b**, in the crystal structure of **2a** also, the bpy and carboxylate of **2** interact with Co(II), forming Co−N and Co−O dative bonds. However, complex **2a** is a dinuclear metal system with a novel coordination arrangement as shown in Figure 4a. The packing arrangement of the coordination units is shown in Figure 4b. In each unit the two Co(II) metal centers are held together by two carboxylates of **2** through Co−O bonds in a bridging fashion with distances of 2.041 and 2.068 Å (Table 2). The topology of Co−O bonds around Co(II) is, in fact, similar to that of the bonds formed in complex **1b**, involving the middle Co(II). Further, this arrangement is reminiscent of the hydrogen-bonded cyclic couplings that are formed between carboxylic acids (see Chart 1b).

Further, each Co(II) completes its 6-fold coordination by interacting with two bpy molecules and one more carboxylate of **2**. The Co−N bonds formed between Co(II) and bpy are linear with distances of 2.156 and 2.157 Å (Table 2). However, the carboxylate interacts with Co(II) as a bidentate ligand and forms chelated Co−O bonds with distances of 2.217 and 2.218 Å (Table 2). A schematic representation of the chelated bonding pattern is shown in Chart 1c. The topological arrangement of organic ligands (**2** and bpy) around Co(II) is very much similar to that of **1a** and **1b**, with the carboxylates occupying equatorial positions and the bpy molecules lying at axial positions of the octahedron. Further, these coordination units form infinite polymer chains through Co−N bonds formed between Co(II) and bpy. These polymer chains in the three-dimensionsional arrangement constitute a channel structure as shown in Figure 4c. A noteworthy feature is that, in complex **2a**, the channels are the result of interaction between the one-dimensional polymer chains connected together by C−H···O hydrogen bonds (H···O distance 2.44−2.95 Å, Figure 4b), unlike similar channel structures known in the literature wherein the channels are created exclusively due to the dative bonds formed between the metal and organic ligands.[9,10,12] However, the occupants of the channels, most probably the solvent molecules (CH_3OH), could not be determined by single-crystal X-ray diffraction methods, unequivocally, as complex **2a** is unstable. However, the calculations reveal that the void space in the channels is 170 Å^3, suggesting the possible presence of methanol molecules. Further, another noteworthy and interesting feature of complex **2a** is that no solvent molecule is coordinated to Co(II), unlike in **1a** and **1b**. This has prompted us to carry out crystallization of **2**, bpy, and cobalt nitrate from different solvents with a hope that pseudopolymorphs would result, replacing the solvent molecules in the crystal lattice of **2a**. However, we were only successful in obtaining a complex from a DMSO solution.

Crystal Structure of $[Co(C_8H_5N_2O_6)_2(C_{10}H_8N_2)_2(H_2O)_2]$-$(CH_3)_2SO$, 2b. The pale pink crystals of **2b**, obtained from DMSO solution, in fact, are found to be quite stable, unlike **2a**. The crystal structure determination, however, reveals the presence of DMSO molecules in the crystal lattice, in which **2**, bpy, and cobalt nitrate are in a 2:1:1 ratio. Following the same trend as observed in **1a**, **1b**, and **2a**, molecules of bpy interact with Co(II) through Co−N bonds with a distance of 2.174 Å and form infinite polymeric chains. We have shown the arrangement of molecules around each metal center and their packing in the three-dimensional arrangement in Figure 5a.

It is evident that two carboxylates of **2** interact with Co(II) in a monodentate manner, with a distance of 2.080 Å. However, the 6-fold coordination around Co(II) is completed with the coordination of two water molecules. So, as was noted in **2a**, no solvent of crystallization (DMSO) molecules coordinated to Co(II). Thus, the octahedron geometry around each Co(II) is achieved with bpy molecules at the apices, with acid molecules and water molecules occupying the equatorial positions.

An interesting feature is that, in contrast to the arrangement of carboxylates in **1a**, **1b**, and **2a**, the two carboxylates in **2b** arrange in a cisoid manner in the basal plane. As a consequence, a bilayered structure is obtained such that carboxylate molecules are embedded between the polymer chains constructed by Co(II) and bpy. This arrangement is shown in Figure 5b. These bilayers stack in three dimensions separated by solvent of crystallization (DMSO) molecules. Calculations of intermolecular interactions reveal that DMSO interacts with the bilayers through O−H···O hydrogen bonds formed between coordinated water molecules and DMSO.

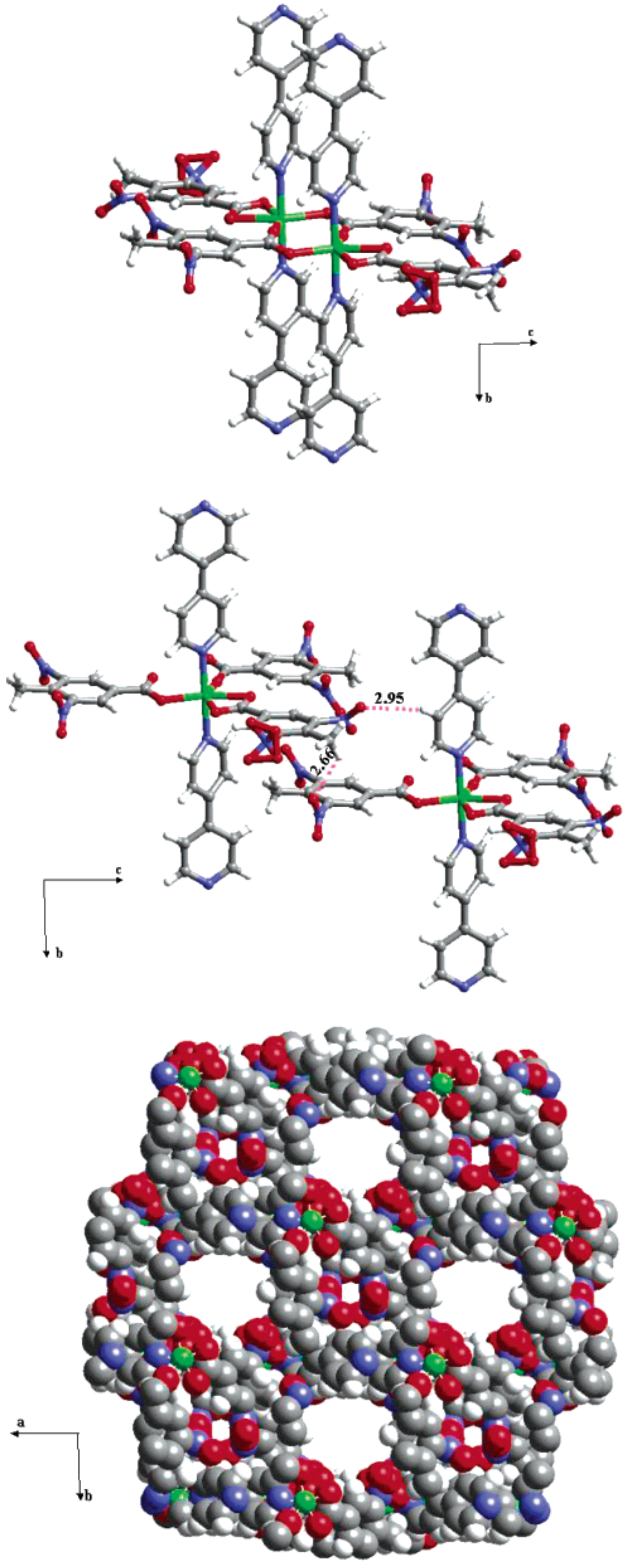


Figure 4. (a, top) Bimetal coordination polymer unit in **2a**. (b, middle) Packing of bimetal coordination polymers in the crystal structure of complex **2a**. (c, bottom) Representation of channels, along a crystallographic direction, observed in **2a**.

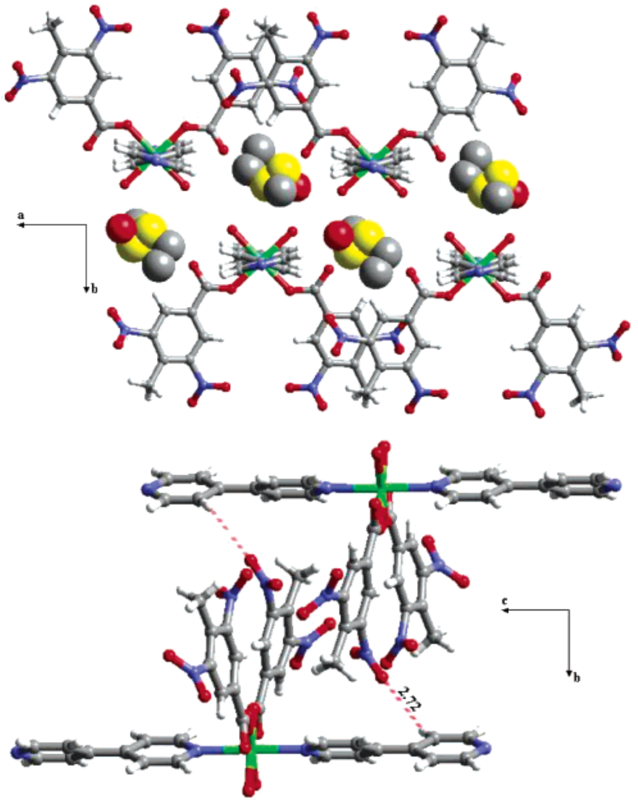
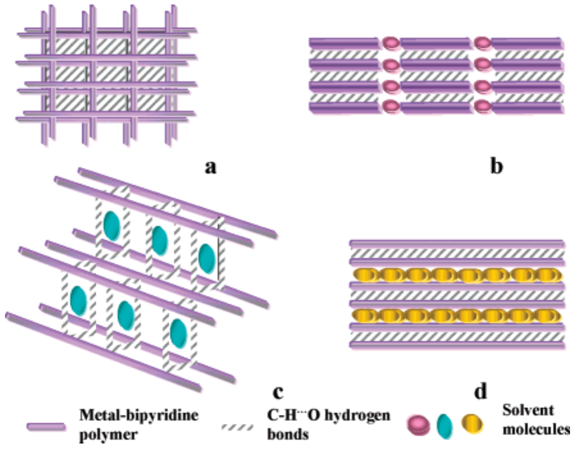


Figure 5. (a, top) Three-dimensional arrangement of coordination polymers in the crystal structure of complex **2b**. (b, bottom) Representation of bilayers with the coordinated acid molecules between the layers.

Chart 2. Representation of the Packing of Polymer Chains in the Crystal Structures of (a) **1a**, (b) **1b**, (c) **2a**, and (d) **2b**



Thus, complex **2b** forms a host−guest-type assembly, which is reminiscent of the well-known clay structures.

Similarities and Contrasts. It is evident from the above discussion of individual structures of complexes **1a**, **1b**, **2a**, and **2b** that these are unique on their own, but a close look at the structures in a collective manner indicates several common features along with differences. The packing arrangement in the crystal structures is schematically represented in Chart 2. First, all the complexes **1a**, **1b**, **2a**, and **2b** form infinite coordination polymer chains due to the interaction between Co(II) and bpy. Further, in all the complexes, the major binding force between the polymer chains is the C−H···O hydrogen bonds formed between the $-NO_2$ groups and hydrogen atoms of bpy.

It is further evident from Chart 2 that in all the complexes the adjacent polymer chains, parallel to each other, are held together by C−H···O hydrogen bonds, except in **1a**. In the crystal structure of **1a**, the C–H···O hydrogen bonds are formed between the polymer chains perpendicular to each other. Further, in all the complexes, octahedral geometry was obtained with bpy molecules lying at the apices and carboxylate molecules in the equatorial positions. Complexes **1a**, **1b**, **2a**, and **2b**, however, also differ from each other, especially in the way the polymer chains are arranged in the three-dimensional space, which is of course influenced by the carboxylate groups. Thus, while **1a** forms a square grid network (Chart 2a), the other complexes, **1b**, **2a**, and **2b**, form host–guest-type structures with the incorporation of solvent molecules. Further, complexes **1b** and **2b** are closely related to each other with the insertion of solvent molecules between the polymer chains. In coordination complex **2a**, however, the solvent molecules occupy the channels created along a crystallographic axis.

In conclusion, we have reported four coordination polymers, **1a**, **1b**, **2a**, and **2b**, formed by **1** and **2** with 4,4′-bipyridine and cobalt nitrate. All the complexes have octahedral arrangement at Co(II). 4,4′-Bipyridine serves as a bismonodentate ligand and bridges adjacent Co(II) metal centers in one dimension to form infinite chains. Formation of different types of coordination linkages by carboxylate groups with the variation of solvent molecules leads to the creation of different topologies such as square grids, channels, and clay-type structures. Except **1a**, all other complexes form void structures, with the solvent molecules occupying the void positions. Also, the geometries of the voids are different due to the differences in the arrangement of the polymer chains. In addition, the observed topologies of Co–O bonds have been correlated with the different types of hydrogen bonds formed by carboxylic acids in organic crystal structures.

Experimental Section

Synthesis of Complexes by Cocrystallization Methods. All the chemicals were obtained commercially, and the crystallization experiments were carried out at room temperature by dissolving the constituent reactants in spectroscopic-grade solvents, as the case may be. The synthesis of each complex is described below.

$[Co(C_7H_3N_2O_6)_2(C_{10}H_8N_2)_2(CH_3O)_2]$, 1a. A solution of **1** (0.106 g, 0.5 mmol) in methanol (10 mL) was slowly added to a warm solution of $Co(NO_3)_2\cdot 6H_2O$ (0.146 g, 0.5 mmol) in methanol (10 mL) with constant stirring over a period of 5 min. To this mixture was added dropwise 4,4′-bipyridine (0.078 g, 0.5 mmol) in methanol (5 mL). The reaction mixture was warmed for a while and allowed to evaporate slowly under ambient conditions. Pale pink needles suitable for X-ray analysis were obtained within 2 days.

$[Co_4(C_7H_3N_2O_6)_8(C_{10}H_8N_2)_8(CH_3O)_2]CH_3COCH_3$, 1b. To a warm solution of $Co(NO_3)_2\cdot 6H_2O$ (0.146 g, 0.5 mmol) in methanol (10 mL) was added slowly with constant stirring the methanolic solution (5 mL) of **1** (0.106 g, 0.5 mmol). To the mixture was added dropwise over a period of 5 min 4,4′-bipyridine (0.078 g, 0.5 mmol) in methanol (5 mL). Acetone (5 mL) was allowed to diffuse slowly through the reaction mixture. Pale pink needles of X-ray quality were obtained over a period of 3 days.

$[Co_2(\mu^2\text{-}C_8H_5N_2O_6)_2(\mu^2\text{-}C_8H_5N_2O_6)_2(C_{10}H_8N_2)_4]$, 2a. $Co(NO_3)_2\cdot 6H_2O$ (0.146 g, 0.5 mmol) in methanol (15 mL) was added dropwise to a solution of acid **2** (0.113 g, 0.5 mmol) in methanol (5 mL). To this stirred solution was added slowly over a period of 5 min 4,4′-bipyridine (0.078 g, 0.5 mmol) in a 1:1 mixture of methanol and acetone (10 mL). Pale pink needles were obtained over a period of 2 days and were found to be suitable for X-ray analysis.

Crystal Structure of $[Co(C_8H_5N_2O_6)_2(C_{10}H_8N_2)_2(H_2O)_2](CH_3)_2SO$, 2b. A solution of **2** (0.113 g, 0.5 mmol) in methanol (10 mL) was added dropwise with constant stirring to a warm solution of $Co(NO_3)_2\cdot 6H_2O$ (0.146 g, 0.5 mmol) in methanol (5 mL). To this reaction mixture was added over a period of 5 min 4,4′-bipyridine (0.078 g, 0.5 mmol) in methanol (10 mL). This reaction mixture was warmed for a while, and DMSO (2 mL) was allowed to diffuse slowly to yield pale pink X-ray-quality crystals.

X-ray Crystallography. Good-quality single crystals of **1a**, **1b**, **2a**, and **2b** were carefully chosen after they were viewed through a Leica microscope supported by a rotatable polarizing stage and a CCD camera. The crystals were glued to a thin glass fiber using an adhesive (cyano acrylate) and mounted on a diffractometer equipped with an APEX CCD area detector. The X-ray intensity data were collected into 2424 frames with varying exposure time (10 s, **1a**; 5 s, **1b** and **2a**; 10 s, **2b**) depending upon the quality and stability of the crystal(s). The data collection was smooth in all the cases, and no extraordinary methods were employed, except that the crystals were smeared in cyano acrylate to protect them from ambient laboratory conditions. The intensity data were processed using Bruker's suite of data processing programs[24] (SAINT), and absorption corrections were applied using SADABS. The structure solution of all the complexes was carried out by direct methods, and refinements were performed by full-matrix least-squares on F^2 using the SHELXTL-PLUS suite of programs. All the structures converged to good R factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms obtained from Fourier maps were refined isotropically. All the refinements were smooth in all the structures. Intermolecular interactions were computed using the PLATON program.[25]

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Supporting Information Available: X-ray data with details of the refinement procedures (CIF files), ORTEP plots, lists of bond parameters (bond lengths and angles), and structure factors of molecular complexes **1a**, **1b**, **2a**, and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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