

Cobalt Complexes Appended with *para*- and *meta*-Arylcarboxylic Acids: Influence of Cation, Solvent, and Symmetry on Hydrogen-Bonded Assemblies

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Supporting Information

ABSTRACT: The present work shows the syntheses, structures, and hydrogen-bonding-based self-assembly of Co^{3+} coordination complexes containing appended arylcarboxylic acid groups. The carboxylic acid groups are present at either the *para* or the *meta* position of the appended arene ring. Every Co^{3+} coordination complex offers both hydrogen-bond donors (in O–H groups of arylcarboxylic acid) and acceptors (in C= O_{amide} groups as well as C= O_{acid} of arylcarboxylic acid) in a single molecule. As a consequence, all molecules self-assemble in a highly complementary



and unique structural fashion via an array of inter- and intramolecular hydrogen bonding. The position of carboxylic acid, presence of cation, type of cation, and solvent of crystallization has significantly affected/altered the self-assembly process of complementary functional groups.

INTRODUCTION

The design and self-assembly of hydrogen bond (H-bond)-containing synthons¹ is an important research activity in supramolecular chemistry.² The motivation for preparing intricate synthetic systems with specific one- (1D), two- (2D), and three-dimensional (3D) architectures³⁻¹⁰ is often inspired from nature where biological molecules self-assemble in unique, yet energetically limited, architectural forms.^{1,2} In addition, research activities are also driven by the requirement of newer materials with structure-specific properties and tailor-made applications.¹¹ One of the major challenges in this field is to understand the parameters that control the molecular self-assembly and thus help the scientific community to take a small, yet vital, step toward predicting the final outcome of the self-assembled architectures.^{3,12} Recent progress in the vast field of supramolecular chemistry is targeted to understand the molecular selfassembly of synthetically designed organic molecules that act as the molecular building blocks and contain H-bond-sensitive functional groups.¹² In addition, significant progress has also been made to look into the coordination-driven self-assemblies where metal-to-ligand bonding generates diverse topological architectures.¹³

The molecular synthons based on carboxylic acid groups have been extremely important and abundant in the self-assembled structures.^{7,12a,b,14} For H-bond-based structures; carboxylic acid groups are quite interesting for several reasons.^{7,12a,14} One of the most important reasons is that such a synthon exhibits dual character as the oxygen atom of the –COOH group can act as an acceptor for H-bonds, whereas the hydroxyl group can act as a donor.^{12a} Therefore, carboxylic acid groups are selfcomplementary in nature and tend to create intermolecularly linked dimers.^{14c} Common binding modes for the carboxylic acids based synthons are cyclic dimers, trimers, and higher polygons, and chains, tapes, and other catemeric motifs.¹⁵ Notably, examples where two carboxylic acid based groups are involved come under the category of homosynthons.¹⁶ However, when a sufficiently polar group, which can potentially form one or more H-bonds, is associated with a carboxylic acid based synthon, it comes under the class of heterosynthons.¹⁷ The main advantage of a heterosynthon-based approach is that several geometrically different building blocks can be easily programmed into supramolecular structures, which are otherwise extremely difficult to achieve with homosynthons. Few intriguing examples show that the heterosynthons can be used to change the dimensionality of carboxylic acids and rationally modulate the periodicity of the pattern.^{17a} Further, in the case of several competing synthons, the self-assembly pattern tends to follow a typical hierarchical principle,¹⁸ that is, the best H-bond donor pairs with the best H-bond acceptor, the second best donor with the second-best acceptor, and so on. The situation becomes more complex, although interesting, when a certain number of water molecules co-crystallize with carboxylic acid based motifs and actively participate and/or compete in the self-assembly. In such instances, a water molecule may act as "glue" and connect two carboxylic acids together, or a water molecule may also function as a "spacer" and elongate the framework.¹⁹ Of course, such a situation again qualifies within the broad domain of heterosynthons.

Our research has been focusing on developing coordination complexes as the building blocks for the construction of ordered structures.²⁰ A coordination complex as the building block offers structural rigidity that has the ability to place the auxiliary functional groups in a preorganized conformation. Such auxiliary functional groups could then be utilized to either coordinate a secondary metal ion or be involved in the self-assembly. The first

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Table 1. Crystallogra _l	phic Data Collectio	on and Refinement Par	ameters for Compl	lexes 1–8				
	1	2	9	4	S	6	7	æ
formula	C ₃₉ H ₂₇ Co N ₆ O ₁₁	$\mathrm{C_{40}H_{27}Cl_2CoN_6O_{11}}$	$C_{50}H_{62}CoN_7O_{20}$	$C_{50}H_{46}C_{0}N_{7}O_{12}$	$\mathrm{C}_{42}\mathrm{H}_{55}\mathrm{CoN}_6\mathrm{O}_{25}$	$\mathrm{C_{42}H_{28}CoN_6O_{15}}$	$C_{45}H_{33}CoN_7O_{17}$	$C_{54}H_{24}CoN_{10}O_{20}$
fw	814.60	897.51	1140.03	995.87	1102.85	915.63	1002.71	1191.75
$T(\mathbf{K})$	298(2)	298(2)	298(2)	298(2)	150(2)	298(2)	150(2)	150(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic	triclinic	triclinic	triclinic	tetragonal
space group	$P2_1/n$	$P\overline{I}$	$P\overline{1}$	$P2_1/n$	$P\overline{I}$	$P\overline{I}$	$P\overline{1}$	$P42_1c$
a (Å)	15.746(5)	11.1233(4)	11.0105(7)	15.4107(8)	11.661(5)	9.151(5)	13.786(5)	13.137(5)
b (Å)	15.494(5)	13.8959(6)	15.6825(11)	19.9408(9)	14.927(5)	15.215(5)	13.876(5)	13.137(5)
c (Å)	18.780(5)	13.9541(5)	17.8843(8)	16.0080(7)	16.137(5)	15.957(5)	15.715(5)	15.308(5)
$\alpha (deg)$	06	$86.470(3)^{\circ}$	111.061(5)	60	109.277(5)	106.780(5)	101.880(5)	90
β (deg)	103.107(5)	$66.757(3)^{\circ}$	103.503(5)	93.073(5)	108.348(5)	96.311(5)	92.772(5)	90
γ (deg)	06	$80.763(3)^{\circ}$	99.944(5)	60	98.360(5)	105.690(5)	118.480(5)	90
$V\left({{{ m{A}}^3}} ight)$	4462(2)	1956.11(13)	2687.8(3)	4912.2(4)	2417.2(15)	2004.8(14)	2548.0(15)	2641.9(17)
Z	4	2	2	4	2	2	2	8
$d ({ m g} { m cm}^{-3})$	1.213	1.524	1.389	1.347	1.512	1.517	1.307	1.493
$\mu/{ m mm}^{-1}$	0.444	0.646	0.402	0.419	0.451	0.510	0.411	0.416
F(000)	1672.0	916	1164	2072	1148	938	1030	1202
$GOF(F^2)$	1.012	1.020	1.048	1.033	1.023	1.115	1.057	1.109
R1, wR ₂ $[I > 2\sigma(I)]$	0.0640, 0.1711	0.0542, 0.1333	0.0587, 0.1559	0.0551, 0.1390	0.0594, 0.1399	0.1386, 0.2565	0.0769, 0.2087	0.0652, 0.1641
R1, wR ₂ (all data) ^{<i>a</i>}	0.0932, 0.1918	0.0614, 0.1384	0.0703, 0.1653	0.0717, 0.1490	0.0845, 0.1511	0.2172, 0.2983	0.0859, 0.2170	0.0689, 0.1671
${}^{a}R_{1} = \sum F_{o} - F_{c} / \sum I $	$^{r}_{o}$; $wR_2 = \{\sum [w(F_o ^2$	${}^{2} - F_{c} ^{2})^{2}] / \sum [wF_{o}^{4}] \}^{1/2}.$						

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synthetic strategy has allowed us to prepare the ${M^{n+}-Co^{3+}-}$ M^{n+} heterobimetallic complexes ($M^{n+} = Zn^{2+}$, Cd^{2+} , Hg^{2+} , and Cu^+)^{20a-c} and { $Co^{3+}-Zn^{2+}$ }^{20e} or { $Co^{3+}-Cd^{2+}$ }^{20f} networks of a highly ordered nature. The second strategy has permitted us to introduce H-bond-based functional groups that have the propensity to self-assemble. In a recent work,²⁰ⁱ we showed the self-assembly of Co3+-based building blocks appended with phenol and catechol groups. An important aspect of this work was that these complexes offered both H-bond donors (in O-H group) as well as acceptors (in O=C_{amide} group) in a single molecule and thus operated in a highly complementary manner. We anticipated that the replacement of a phenol group by carboxylic acid may lead to a more complex situation as a -COOH group exhibits dual character and offers both H-bond acceptor and donor.^{14a,b} Herein, we report several Co³⁺ complexes appended with p- and m-carboxylic acids as the building blocks to understand their self-assembly through hydrogen bonding (H-bonding). We also attempt to understand the effect of cations, solvent of crystallization, and symmetry on the self-assembly process.

EXPERIMENTAL SECTION

Materials and Methods. Reagents of analytical grade were procured from Sigma-Aldrich, Alfa-Aesar, and Spectrochem and were used without further purification. The solvents were purified using standard literature methods.²¹

Synthesis of Ligands. 2-(4-Ethylbenzoate-carbomyl)pyridine (HBL^{p-COOEt}). Pyridine-2-carboxylic acid (1.0 g, 0.08 mmol) was added as a solid in one portion to a suspension of ethyl-4-amino benzoate (1.35 g, 0.08 mmol) in pyridine (10 mL), and the mixture was stirred at 40 °C for 40 min. Triphenylphosphite (5.89 g, 0.019 mmol) was added dropwise over 10 min to the aforementioned mixture, and the temperature was increased to 90 °C. The reaction mixture was stirred for 4 h at 90 °C. On cooling to room temperature, a colorless precipitate was obtained that was filtered, washed with water, and dried. The crude product was purified by recrystallization with aqueous CH₃OH. Yield: 2.02 g, 92%. Anal. Calcd for C15H14N2O3: C, 66.66%; H, 5.22%; N, 10.36%. Found: C, 66.62%; H, 5.38%; N, 10.54%. FTIR (KBr, selected peaks): 3336 (N-H), 1712 (COO), 1543 (C=O) cm⁻¹. ¹H NMR $(CDCl_3, 400 \text{ MHz}): \delta = 10.23 \text{ (s, 2H, CONH), } 1.39 \text{ (s, 3H, H}_1\text{), } 4.37$ (q, 2H, H₂), 8.09 (d, 1H, H₅), 7.87 (d, 1H, H₆), 8.31 (d, 1H, H₁₀), 7.93-8.07 (m, 1H, H_{11}), 7.53 (m, 1H, H_{12}), 8.63 (d, 1H, H_{13}). ¹³C NMR $(CDCl_3, 400 \text{ MHz}): \delta = 14.33 (C_1), 60.82 (C_2), 166.14 (C_3), 148.00$ (C₄), 122.50 (C₅), 118.80 (C₆), 137.78 (C₇), 162.16 (C₈), 149.29 (C₉), 126.74 (C₁₀), 130.82 (C₁₁), 125.96 (C₁₂), 141.70 (C₁₃). 2-(3-Ethylbenzoate-carbomyl)pyridine (HBL^{m-COOEt}). This ligand

2-(3-Ethylbenzoate-carbomyl)pyridine (HBL^{mCODEI}). This ligand was synthesized in a similar manner as that of HBL^{p-CODEt} using ethyl-3-amino benzoate in place of ethyl-4-amino benzoate. Yield: 1.90 g, 87%. Anal. Calcd for C₁₅H₁₄N₂O₃: C, 66.66%; H, 5.22%; N, 10.36%. Found C; 66.38%; H, 5.47%; N, 10.31%. FTIR (KBr, selected peaks): 3336 (N-H), 1713 (COO), 1696, 1612 (C=O) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 10.14 (s, 2H, CONH), 1.40 (t, 3H, H₁), 4.39 (q, 2H, H₂), 7.25 (m, 1H, H₅), 7.48 (m, 1H, H₆), 6.82 (d, 1H, H₇), 8.62 (s, 1H, H₉), 7.81 (d, 1H, H₁₂), 8.27 (m, 1H, H₁₃), 7.91 (m, 1H, H₁₄), 8.22 (d, 1H, H₁₅). ¹³C NMR (CDCl₃, 400 MHz): δ = 14.33 (C₁), 61.16 (C₂), 166.18 (C₃), 148.02 (C₄), 122.46 (C₅), 115.22 (C₆), 120.55 (C₇), 137.86 (C₈), 126.64 (C₉), 162.20 (C₁₀), 149.62 (C₁₁), 123.96 (C₁₂), 129.21 (C₁₃), 125.37 (C₁₄), 131.35 (C₁₅).

2,6-Bis(4-methylbenzoate-carbomyl)pyridine ($H_2L^{p-COOMe}$). This ligand was also synthesized in a similar manner using pyridine-2, 6-dicarboxylic acid and methyl-4-amino benzoate in a 1:2 ratio. The crude product was recrystallized from aqueous CH₃OH. Yield: 2.54 g, 98%. Anal. Calcd for C₂₃H₁₉N₃O₆·2H₂O: C, 58.85%; H, 4.94%; N, 8.95%. Found: C, 58.74%; H, 5.18%; N, 9.03%. FTIR (KBr, selected peaks): 3337 (NH), 1714, 1686 (COO), 1665 (C=O) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 9.62 (s, 2H, CONH), 3.94 (s, 6H, H₁/H₁'), 7.88 (d, 4H, H₄/H₄'), 8.14 (d, 4H, H₅/H₅'), 8.56 (d, 2H, H₉/H₉', J = 8 Hz), 8.21 (t, 1H, H₁₀). ¹³C NMR (CDCl₃, 400 MHz): δ = 51.99 (C₁), 166.46(C₂), 126.42 (C₃), 131.06 (C₄), 119.31 (C₅), 140.97 (C₆), 160.98 (C₇), 148.60 (C₈), 126.17 (C₉), 139.90 (C₁₀).

2,6-Bis(3-ethylbenzoate-carbomyl)pyridine ($H_2L^{m-COOEt}$). This ligand was synthesized similarly using ethyl-3-amino benzoate in place of methyl-4-amino benzoate. Yield: 2.46 g, 89%. Anal. Calcd for C₂₅H₂₃N₃O₆·H₂O: C, 62.62%; H, 5.26%; N, 8.76%. Found: C, 62.70%; H, 5.38%; N, 8.65%. FTIR (KBr, selected peaks): 3334 (NH), 1702 (COO), 1686 (C=O) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =10.60 (s, 2H, CONH), 1.10 (t, 6H, H₁/H₁'), 4.06 (q, 4H, H₂/H₂'), 7.70 (d, 2H, H₅/H₅', *J* = 8 Hz), 7.40 (m, 2H, H₆/H₆'), 8.20 (d, 2H, H₇/H₇'), 8.48 (s, 2H, H₉/H₉'), 8.52 (d, 2H, H₁₂/H₁₂'), 8.54 (t, 1H, H₁₃). ¹³C NMR (CDCl₃, 400 MHz): δ = 14.17 (C₁), 60.80 (C₂), 166.26 (C₃), 130.30 (C₄), 125.42 (C₅), 128.99 (C₆), 124.10 (C₇), 137.78 (C₈), 122.11 (C₉), 161.29 (C₁₀), 148.78 (C₁₁), 125.28 (C₁₂), 139.63 (C₁₃).

Synthesis of Cobalt(III) Complexes with Protected Carboxylic Acid Groups. $[Co(BL^{p-COOEt})_3]$ (1^{*P*}). The ligand HBL^{*p*-COOEt} (0.50 g, 1.85 mmol) was dissolved in dinitrogen-flushed DMF and treated with solid NaH (44.4 mg, 1.85 mmol). The resulting mixture was then stirred for 30 min at room temperature, and solid $[Co(H_2O)_6](ClO_4)_2$ (223.2 mg, 0.61 mmol) was added to the aforementioned mixture. After 30 min of stirring, dry O₂ was purged to the solution for 2 min. The solution was finally stirred for 1 h. The reaction mixture was filtered, followed by the removal of the solvent under reduced pressure. The crude product was isolated after washing with diethyl ether. The crude product thus obtained was dissolved in DMF and subjected to vapor diffusion of diethyl ether, which afforded a crystalline product within 2 days. Yield: 1.2 g, 75%. Anal. Calcd for C₄₅H₃₉N₆O₉Co·6H₂O: C, 55.44%, H, 5.27%, N, 8.52%. Found: C, 55.81%; H, 5.41%; N, 8.06%. FTIR (KBr, selected peaks): 3426 (OH), 1717, 1664 (COO), 1636, 1593 (C=O) cm⁻¹. Absorption spectrum $[\lambda_{max}, nm, CH_3OH(\epsilon, M^{-1} cm^{-1})]$: 640 (40), 530 (sh, 270), 500 (sh, 310). Conductivity (~1 mM, CH₃OH, 298 K): $\Lambda_{\rm M}$ = 8 Ω^{-1} cm² mol⁻¹ (the range for 1:1 electrolyte in CH₃OH is 80–115). ¹H NMR (CDCl₃, 400 MHz): $\delta = 1.31 - 1.35$ (m, 9H, H₁), 4.30-4.23 (m, 6H, H₂), 7.23–7.25 (m, 3H, H₅ protons for three asymmetric ligands), 7.02, 6.52, 6.22 (br, 3H, H₆), 7.93–7.96 (t, 3H, H₁₀ protons for three asymmetric ligands), 7.70, 7.85 (m/m, 3H, H_{11} protons for three asymmetric ligands), 7.64, 7.41 (d, 3H, H₁₂ protons for three asymmetric ligands), 9.07, 8.60, 8.38 (d, 3H, H₁₃ protons for three asymmetric ligands).

[Co(BL^{m-COOEt})₃] (**2**^{*P*}). This complex was synthesized using an identical scale in a similar manner as that of complex **1**^{*P*} using ligand HBL^{m-COOOEt} in place of HBL^{*p*-COOOEt}. Yield: 0.98 g, 62%. Anal. Calcd for C₄₅H₃₉N₆O₉Co·2H₂O: C, 59.87%, H, 4.80%, N, 9.31%. Found: C, 59.47%; H, 4.46%; N, 9.11%. FTIR (KBr, selected peaks): 3433 (OH), 1718, (COO), 1600 (C=O) cm⁻¹. Absorption spectrum [λ_{max} , nm, CH₃OH (ε , M⁻¹ cm⁻¹)]: 655 (30), 525 (sh, 190), 500 (sh, 225). Conductivity (~1 mM, CH₃OH, 298 K): $\Lambda_{\rm M}$ = 5 Ω⁻¹ cm² mol⁻¹ (the range for 1:1 electrolyte in CH₃OH is 80–115). ¹H NMR (CDCl₃, 400 MHz): δ =1.17–1.26 (m, 9H, H₁), 4.24–4.26 (m, 6H, H₂), 7.86, (m, 3H, H₅), 6.80, 6.85 (m, 3H, H₆), 7.70 (m, 3H, H₇ protons for three asymmetric ligands), 7.18, 7.28 (m, 3H, H₁₄ protons for three asymmetric ligands), 7.18, 7.28 (m, 3H, H₁₅ protons for three asymmetric ligands). (*Et*₄*N*)[*Co*(*L*^{*p*-COOMe})₂] (**3**^{*P*}). The ligand H₂L^{*p*-COOMe} (1.0 g, 2.30 mmol)

 $(Et_4N)[Co(L^{p-COOMe})_2]$ (3^{*P*}). The ligand H₂L^{*p*-COOMe} (1.0 g, 2.30 mmol) was dissolved in CH₂Cl₂ (50 mL), and to it was added Co(OAc)₂·4H₂O (0.287 g, 1.15 mmol) and K₂CO₃ (7.99 g, 57.88 mmol). The resulting mixture was refluxed for 4 h. To the resulting yellow-red solution was added solid Et₄NCl·*x*H₂O (0.764 g, 4.62 mmol), and stirring was continued for an additional 2 h at room temperature in open air. Exposure to air resulted in a dark coloration of the solution. Subsequently, solvent was removed under reduced pressure, followed by the addition of CH₃CN. The solution was filtered, and the filtrate was concentrated to ¹/₄th of its original volume. Addition of diethyl ether resulted in the isolation of a dark green precipitate, which was filtered and dried in vacuum. The compound was recrystallized by diffusing the vapors of Et₂O to a CH₃CN solution of the crude product. Yield: 1.4 g, 58%. Anal. Calcd for C₅₄H₅₄CoN₇O₁₂·2H₂O: C, 59.61; H, 5.37; N, 9.01;

Found: C, 59.14%; H, 4.97%; N, 8.77%. FTIR (KBr, selected peaks): 3448 (OH), 1718 (COO), 1611 (C=O) cm⁻¹. Conductivity (CH₃CN, ~1 mM solution at 298 K): $\Lambda_{\rm M} = 125 \,\Omega^{-1} \,{\rm cm}^2 \,{\rm mol}^{-1}$ (the range for 1:1 electrolyte in CH₃CN is 120–160). Absorption spectrum ($\lambda_{\rm max}$, nm, CH₃OH (ε , M⁻¹ cm⁻¹): 651 (160), 568 (sh, 60). ¹H NMR (CDCl₃, 400 MHz): $\delta = 3.80$ (s, 12H, H₁/H₁'), 6.92 (d, 8H, H₄/H₄', *J* = 8 Hz), 7.58 (d, 8H, H₅/H₅', *J* = 8 Hz), 7.70 (d, 4H, H₉/H₉', *J* = 8 Hz), 7.83 (t, 2H, H₁₀), 3.02 (q, 8H, -CH₂-, Et₄N⁺), 1.15 (t, 12H, -CH₃, Et₄N⁺). ¹³C NMR (CDCl₃, 400 MHz): $\delta = 7.50$ (-CH₃, Et₄N⁺), 51.99 (-CH₂-, Et₄N⁺), 52.48 (C₁), 167.44 (C₂), 139.21 (C₃), 124.36 (C₄), 125.70 (C₅), 150.65 (C₆), 167.12 (C₇), 156.33 (C₈), 126.41 (C₉), 129.90 (C₁₀).

(*Et₄N*)[*Co*(*L*^{*m*-COOEt})₂] (**4**^{*P*}). The complex **4**^{*P*} was synthesized using an identical scale and method as that of **3**^{*P*}, however, using ligand H₂L^{*m*-COOEt} in place of H₂L^{*p*-COOMe}. Yield: 1.36 g, 57%. Anal. Calcd for C₅₈H₆₂CoN₇O₁₂·6H₂O: C, 57.28; H, 6.13; N, 8.06. Found: C, 57.01%; H, 6.56%; N, 7.71%. FTIR (KBr, selected peaks): 3422 (OH), 1718 (COO), 1618 (C=O) cm⁻¹. Conductivity (CH₃CN, ~1 mM solution at 298 K): Λ_M = 145 Ω⁻¹ cm² mol⁻¹ (the range for 1:1 electrolyte in CH₃CN is 120–160). Absorption spectrum (λ_{max} nm, CH₃OH (*ε*, M⁻¹ cm⁻¹): 631 (60), 562 (sh, 30). ¹H NMR (CDCl₃, 400 MHz): δ = 1.28 (t, 12H, H₁/H₁·), 4.18 (q, 8H, H₂/H₂·), 7.15 (d, 4H, H₅/H₅·), 6.98 (m, 4H, H₆/H₆), 7.48 (d, 4H, H₇/H₇·), 7.34 (s, 4H, H₉/H₉·), 7.62 (d, 4H, H₁₂/H₁₂·), 7.71 (t, 2H, H₁₃), 3.22 (q, 8H, −CH₂−, Et₄N⁺), 1.18 (t, 12H, −CH₃, Et₄N⁺), 14.23 (C₁), 60.59 (C₂), 167.30 (C₃), 138.34 (C₄), 125.02 (C₅), 123.94 (C₆), 128.29 (C₇), 145.57 (C₈), 126.87 (C₉), 167.16 (C₁₀), 156.23 (C₁₁), 130.34 (C₁₂), 131.35 (C₁₃).

Na[*Co*(*L*^{*P*-COOMe})₂] (**5**^{*P*}). This compound was synthesized in a similar manner as discussed for **1**^{*P*} using the following reagents: H₂L^{*P*-COOMe} (0.50 g, 1.153 mmol), NaH (0.055 g, 2.307 mmol), and [Co(H₂O)₆]-(ClO₄)₂] (0.211 g, 0.58 mmol). Yield: 0.57 g, 53%. Anal. Calcd for C₄₆H₃N₆O₁₂CoNa·H₂O: C, 57.39%; H, 3.77%; N, 8.73%. Found: C, 57.13%; H, 3.97%; N, 8.98%. FTIR (KBr, selected peaks): 3405 (OH), 1709 (COO), 1608, 1587 (C=O) cm⁻¹. Absorption spectra (λ_{max} nm, DMF (ε , M⁻¹ cm⁻¹): 630 (190), 565 (sh, 140), 545 (sh, 170). Conductivity (~1 mM, CH₃OH, 298 K): Λ_M = 90 Ω⁻¹ cm² mol⁻¹ (the range for 1:1 electrolyte in CH₃OH is 80–115). ¹H NMR (DMSO-*d₆*, 400 MHz): 3.75 (s, 12H, H₁/H₁'), 7.48 (m, 8H, H₄/H₄', *J* = 8 Hz), 6.76 (d, 8H, H₅/H₅', *J* = 8 Hz), 7.67 (d, 4H, H₉/H₉'), 8.02 (t, 2H, H₁₀/H₁₀'). ¹³C NMR (DMSO-*d₆*, 400 MHz): $\delta = 51.91$ (C₁), 166.45 (C₂), 151.05 (C₃), 124.58 (C₄), 123.88 (C₅), 140.11 (C₆), 166.04 (C₇), 155.66 (C₈), 126.39 (C₉), 128.93 (C₁₀). *Na*[*Co*(*L*^{*m*-COOEt}]₂] (**6**^{*P*}). This compound was synthesized in a similar

Na[*Co*(*L*^{*m*-COOEI})₂] (**6**^{*P*}). This compound was synthesized in a similar manner as discussed for **1**^P using the following reagents: H₂*L*^{*m*-COOEt} (0.50 g, 1.083 mmol), NaH (0.057 g, 2.38 mmol), and [Co(H₂O)₆]-(ClO₄)₂] (0.198 g, 0.54 mmol). Yield: 0.54 g, 50%. Anal. Calcd for C₅₀H₄₂N₆O₁₂CoNa·H₂O: C, 58.94%; H, 4.35%; N, 8.25%. Found: C, 58.62%; H, 4.59%; N, 8.41%. FTIR (KBr, selected peaks): 3404 (OH), 1709 (COO), 1609, 1593 (C=O) cm⁻¹. Absorption spectra (λ_{max} nm, CH₃OH (ε , M⁻¹ cm⁻¹): 630 (120), 560 (sh, 80), 550 (sh, 90). Conductivity (~1 mM, CH₃OH, 298 K): Λ_M = 105 Ω⁻¹ cm² mol⁻¹ (the range for 1:1 electrolyte in CH₃OH is 80–115). ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 1.28 (t, 12H, H₁/H₁'), 4.19 (q, 8H, H₂/H₂'), 6.96 (d, 4H, H₅/H₅'), 7.02 (m, 4H, H₆/H₆'), 6.90 (d, 4H, H₇/H₇', *J* = 8 Hz), 7.43 (s, 4H, H₉/H₉'), 7.60 (d, 4H, H₁₂/H₁₂'), 7.94 (t, 2H, H₁₃/H₁₃'). ¹³C NMR (DMSO-*d*₆, 400 MHz): 14.05 (C₁), 60.52 (C₂), 166.40 (C₃), 139.46 (C₄), 127.96 (C₅), 122.89 (C₆), 123.42 (C₇), 145.96 (C₈), 126.29 (C₉), 165.36 (C₁₀), 155.39 (C₁₁), 129.72 (C₁₂), 131.10 (C₁₃).

Synthesis of Cobalt(III) Complexes with Deprotected Carboxylic Acid Groups. $[Co(BL^{p-COOH})_3]$ (1). The complex 1 was obtained after the base-catalyzed deprotection of complex 1^P. The compound 1^P was dissolved in a mixture of THF/H₂O (3:1, v/v) and treated with 3 equiv of NaOH. The reaction mixture was stirred for 12 h at room temperature. The resulting solution was neutralized by 3 N HCl. Removal of THF under vacuum resulted in the precipitation of the product. The crude product was recrystallized from water, which produced a highly crystalline product within 2–3 days. Yield: 0.12 g, 66%. Anal. Calcd for C₃₉H₂₇N₆O₉Co·3H₂O: C, 56.99; H, 3.98; N, 10.04. Found: C, 56.66%; H, 4.16%; N, 10.08%. FTIR (KBr, selected peaks): 3402 (OH), 1702 (COO), 1581 (C=O) cm⁻¹. Conductivity (CH₃OH,

~1 mM, 298 K): $\Lambda_{\rm M}$ = 10 Ω^{-1} cm² mol $^{-1}$ (the range for 1:1 electrolyte in CH₃OH is 80–115). Absorption spectrum ($\lambda_{\rm max}$ nm, CH₃OH (ε , M^{-1} cm $^{-1}$): 645 (30), 525 (sh, 250), 485 (sh, 290). ¹H NMR (DMSO- $d_{6^{\prime}}$ 400 MHz): δ = 7.46–7.52 (m, 6H, H₃ protons for three asymmetric ligands), 7.23, 7.02, 6.24 (d, 6H, H₄ protons for three asymmetric ligands), 7.90–7.94 (m, 3H, H₈ protons for three asymmetric ligands), 8.33, 8.02 (m, 3H, H₉ protons for three asymmetric ligands), 7.67 (d, 3H, H₁₀ protons for three asymmetric ligands), 8.92, 8.73, 8.02 (d, 3H, H₁₁ protons for three asymmetric ligands).

[Co(*BL*^{m-COOH})₃] (2). This compound was synthesized in a similar manner as discussed for complex 1. Yield: 0.096 g, 53%. Anal. Calcd for C₃₉H₂₇CoN₆O₉·CH₂Cl₂: C, 55.38; H, 3.37; N, 9.69. Found: C, 55.12%; H, 3.41%; N, 10.09%. FTIR (KBr, selected peaks): 3422 (OH), 1702 (COO), 1605 (C=O) cm⁻¹. Conductivity (CH₃OH, ~1 mM, 298 K): $\Lambda_{\rm M}$ = 15 Ω^{-1} cm² mol⁻¹ (the range for 1:1 electrolyte in CH₃OH is 80–115). Absorption spectrum ($\lambda_{\rm max}$, nm, CH₃OH (ε , M⁻¹ cm⁻¹): 645 (25), 540 (sh, 190), 505 (230). ¹H NMR (CDCl₃, 400 MHz): δ = 5.30 (s, 2H, CH₂Cl₂), 7.04, 6.79 (m/br, 3H, H₃ protons for three asymmetric ligands), 7.46 (s, 3H, H₇ protons for three asymmetric ligands), 7.32–7.38 (d/d, 6H, H₁₀/H₃ protons for three asymmetric ligands), 8.32 (t, 3H, H₁₁ protons for three asymmetric ligands), 8.95, 8.72, 8.16 (d, 3H, H₁₃ protons for three asymmetric ligands). (*Et₄N)*[Co(L^{*p*-COOH})₂] (3). The complex 3 was synthesized in a similar

manner as that of complex 1. Yield: 0.48 g, 51%. Anal. Calcd for C₅₀H₄₆CoN₇O₁₂·8H₂O: C, 52.68; H, 5.48; N, 8.60. Found: C, 52.42%; H, 5.65%; N, 8.58%. FTIR (KBr, selected peaks): 3404 (OH), 1702 (COO), 1570 (C=O) cm⁻¹. Conductivity (DMF, ~1 mM solution at 298 K): $\Lambda_{\rm M}$ = 70 Ω^{-1} cm² mol⁻¹ (the range for 1:1 electrolyte in DMF is 65–160). Absorption spectrum (λ_{max} nm, CH₃OH (ϵ , M⁻¹ cm⁻¹): 660 (120), 594 (sh, 80). ¹H NMR (DMSO- d_6 , 400 MHz): δ = 12.7 (br, 4H, -COOH), 6.73 (d, 8H, H₃/H₃', J = 8 Hz), 7.45 (d, 8H, H₄/H₄', J = 9 Hz), 7.64 (d, 4H, $H_8/H_{8'}$, J = 8 Hz), 7.99 (t, 2H, H_9), 3.16 (q, 8H, -CH₂-, Et₄N⁺), 1.12 (t, 12H, -CH₃, Et₄N⁺). ¹H NMR (DMSO-d₆/ D_2O_1 400 MHz): $\delta = 6.73$ (d, 8H, $H_3/H_{3'}$, J = 8 Hz), 7.45 (d, 8H, $H_4/$ $H_{4'}$, J = 9 Hz), 7.65 (d, 4H, $H_8/H_{8'}$, J = 8 Hz), 8.02 (t, 2H, H_9), 3.16 (q, 8H, -CH₂-, Et₄N⁺), 1.12 (t, 12H, -CH₃, Et₄N⁺). ¹³C NMR (DMSO d_{6} 400 MHz): $\delta = 17.05 (-CH_3, Et_4N^+), 51.35 (-CH_2-, Et_4N^+),$ 167.14 (C₁), 139.99 (C₂), 123.85 (C₃), 125.71 (C₄), 150.63 (C₅), 166.39 (C₆), 155.77 (C₇), 126.15 (C₈), 129.09 (C₉).

 $(Et_4N)[Co(L^{m-COOH})_2]$ (4). This complex was again synthesized in a similar manner as that noted for complex 1. Yield: 0.54 g, 60%. Anal. Calcd for C50H46CoN7O12: C, 60.30; H, 4.66; N, 9.85. Found: C, 59.95%; H, 4.96%; N, 9.62%. FTIR (KBr, selected peaks): 3427 (OH), 1718 (COO), 1570 (C=O) cm⁻¹. Conductivity (DMF, ~ 1 mM solution at 298 K): $\Lambda_{\rm M}$ = 75 $\Omega^{-1}\, cm^2\, mol^{-1}$ (the range for 1:1 electrolyte in DMF is 65–160). Absorption spectrum (λ_{max} nm, CH₃OH (ϵ , M⁻¹ cm⁻¹): 646 (130), 572 (sh, 60). ¹H NMR (DMSO-*d*₆, 400 MHz): $\delta = 12.57$ (br, 4H, -COOH), 6.90 (d, 4H, H₃/H_{3'}), 6.99 (m, 4H, H₄/H_{4'}), 7.41 (d, 4H, $H_5/H_{5'}$, J = 8 Htz), 7.24 (s, 4H, $H_7/H_{7'}$), 7.53 (d, 4H, H_{10}/H_{10}) $H_{10'}$, J = 8 Hz), 7.91 (t, 2H, H_{11}), 3.18 (q, 8H, $-CH_2$ -, Et_4N^+), 1.13 (t, 12H, $-CH_3$, Et_4N^+). ¹H NMR (DMSO- d_6/D_2O , 400 MHz): $\delta = 6.89$ $(d, 4H, H_3/H_{3'}), 7.00 (m, 4H, H_4/H_{4'}), 7.41 (d, 4H, H_5/H_{5'}, J = 8 Hz),$ 7.27 (s, 4H, $H_7/H_{7'}$), 7.53 (d, 4H, $H_{10}/H_{10'}$, J = 8 Hz), 7.91 (t, 2H, H_{11}), 3.15 (q, 8H, $-CH_2$ -, Et_4N^+), 1.11 (t, 12H, $-CH_3$, Et_4N^+). ¹³C NMR (DMSO- d_{6} , 400 MHz): δ = 7.05 (-CH₃, Et₄N⁺), 51.32 (-CH₂-, Et₄N⁺), 166.85 (C₁), 124.39 (C₂), 127.68 (C₃), 130.46 (C₄), 127.12 (C₅), 139.29 (C₆), 123.45 (C7), 166.54 (C₈), 155.74 (C₉), 130.66 (C₁₀), 145.99 (C₁₁).

 $H_3O^+[Co(L^{p-COOH})_2]$ (5). This complex was obtained after the basecatalyzed deprotection of complex S^P (Na⁺ salt) as follows: Compound S^P was dissolved in a mixture of THF/H₂O (3:1, v/v) and treated with 4 equiv of NaOH. The reaction mixture was stirred for 12 h at room temperature. The resulting solution was neutralized by 4 N HCl. Removal of THF under vacuum resulted in the precipitation of the product. The crude product was recrystallized from water, which produced a highly crystalline product within 4–5 days. Yield: 0.16 g, 55%. Anal. Calcd for $C_{42}H_{29}N_6O_{13}Co-11H_2O$: C, 46.59%; H, 4.75%; N, 7.76%. Found: C, 46.90; H, 4.59; N, 7.65. FTIR (KBr, selected peaks): 3402 (OH), 1702 (COO), 1604 (C=O) cm⁻¹. Conductivity (CH₃OH, ~1 mM solution at 298 K): $\Lambda_{\rm M} = 105 \,\Omega^{-1} \,{\rm cm}^2 \,{\rm mol}^{-1}$ (the range for 1:1 electrolyte in CH₃OH is 80–115). Absorption spectrum ($\lambda_{\rm max}$, nm, CH₃OH (ε , M⁻¹ cm⁻¹): 630 (120), 560 (sh, 65), 540 (sh, 95). ¹H NMR (DMSO- d_{ω} , 400 MHz): $\delta = 6.72$ (d, 8H, H₃/H₃", *J* = 8 Hz), 7.45 (d, 8H, H₄/H₄", *J* = 8 Hz), 7.64 (d, 4H, H₈/H₈", *J* = 8 Hz), 7.98 (t, 2H, H₉/H₉). ¹³C NMR (DMSO- d_{ω} , 400 MHz): $\delta = 167.23$ (C₁), 150.56 (C₂), 125.44 (C₃), 123.77 (C₄), 140.00 (C₅), 166.48 (C₆), 155.80 (C₇), 125.99 (C₈), 129.05 (C₉).

 $H_3O^+[Co(L^{m-COOH})_2]$ (6). This complex was again synthesized in a similar manner as that noted for complex 5. Yield: 0.16 g, 60%. Anal. Calcd for $C_{42}H_{29}N_6O_{13}Co\cdot 2H_2O$: C, 54.79%; H, 3.61%; N, 9.13%. Found: C, 54.57%; H, 3.35%; N, 9.32%. FTIR (KBr, selected peaks): 3410 (OH), 1712, 1690 (COO), 1604, 1582 (C=O) cm⁻¹. Conductivity (CH₃OH, ~1 mM solution at 298 K): $\Lambda_M = 85 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ (the range for 1:1 electrolyte in CH₃OH is 80–120). Absorption spectrum (λ_{max} , nm, CH₃OH (ε , M⁻¹ cm⁻¹): 625 (100), 560 (sh, 60), 545 (sh, 75). ¹H NMR (DMSO- d_{60} , 400 MHz): $\delta = 6.90$ (d, 4H, $H_3/H_{3'}$), 6.99 (d, 4H, H_4/H_4'), 7.41 (d, 4H, $H_5/H_{5'}$, $J = 8 \ Hz$), 7.24





"Conditions: (a) NaH, DMF, N₂; (b) $[Co(H_2O)_6](ClO_4)_2$; (c) excess O₂; (d) NaOH.

 $\begin{array}{l} (d, 4H, H_7/H_7'), 7.54 (d, 4H, H_{10}/H_{10'}, J = 8 \text{ Hz}), 7.92 (t, 2H, H_{11}/H_{11'}).\\ {}^{13}\text{C NMR} (DMSO-d_6, 400 \text{ MHz}): \delta = 166.84 (C_1), 145.96 (C_2), 127.60 \\ (C_3), 123.39 (C_4), 127.13 (C_5), 139.41 (C_6), 130.38 (C_7/C_{11}), 166.56 \\ (C_8), 155.79 (C_9), 124.56 (C_{10}).\\ H_3O^+[Co(L^{P-COOH})_2] (7). \text{ This complex was again synthesized in a} \end{array}$

*H*₃O⁺[*Co*(*L*^{*p*-CO(*H*)}₂] (7). This complex was again synthesized in a similar manner as that noted for complex 5. However, recrystallization was achieved by the vapor diffusion of diethyl ether to a DMF solution of crude complex. Yield: 0.14 g, 50%. Anal. Calcd for C₄₂H₂₉CoN₆O₁₃. 2H₂O·DMF: C, 54.39%; H, 4.06%; N, 9.87%. Found: C, 54.68%; H, 4.33%; N, 9.70%. FTIR (KBr, selected peaks): 3404 (OH), 1702 (COO), 1604 (C=O) cm⁻¹. Conductivity (CH₃OH, ~1 mM solution at 298 K): $\Lambda_{\rm M} = 110 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}$ (the range for 1:1 electrolyte in CH₃OH is 80–115). Absorption spectra ($\lambda_{\rm max}$ nm, CH₃OH (ε , M⁻¹ cm⁻¹): 625 (95), 560 (sh, 50), 545 (sh,70). ¹H NMR (DMSO-d₆/400 MHz): $\delta = 7.94$ (s, 1H, -CHO, DMF), 7.45 (d, 8H, H₃/H₃, *J* = 8 Hz), 6.73 (d, 4H, H₄/H₄, *J* = 8 Hz), 7.65 (d, 4H, H₈/H₈, *J* = 8 Hz), 8.00 (t, 2H, H₉/H₉, *J* = 8 Hz). ¹³C NMR (DMSO-d₆/400 MHz): $\delta = 162.30$ (-CHO, DMF), 167.11 (C₁), 150.58 (C₂), 123.86 (C₃), 125.68 (C₄), 139.96 (C₅), 166.45 (C₆), 155.74 (C₇), 126.11 (C₈), 129.10 (C₉), 30.69 (CH₃, DMF), 34.35 (CH₃⁻ DMF). $H_3O^+[Co(L^{m-COOH})_2]$ (8). This complex was again synthesized in a

*H*₃O⁺[*Co*(*L^{m-COOH*)₂] (**8**). This complex was again synthesized in a similar manner as that mentioned for complex 7. Yield: 0.15 g, 57%. Anal. Calcd for C₄₂H₂₉CoN₆O₁₃·2H₂O·DMF: C, 54.39%; H, 4.06%; N, 9.87%. Found: C, 54.19%; H, 4.27%; N, 9.73%. FTIR (KBr, selected peaks): 3425 (OH), 1702 (COO), 1584 (C=O), cm⁻¹. Conductivity (CH₃OH, ~1 mM solution at 298 K): Λ_M = 95 Ω⁻¹ cm² mol⁻¹ (the range for 1:1 electrolyte in CH₃OH is 80–115). Absorption spectra (λ_{max} nm, CH₃OH (ε , M⁻¹ cm⁻¹): 640 (90), 585 (sh, 75), 570 (85). ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 7.92 (s, 1H, –CHO, DMF), 6.92 (d, 4H, H₃/H_{3'}), 6.98 (t, 4H, H₄/H_{4'}), 7.42 (d, 4H, H₅/H_{5'}, *J* = 8 Hz), 7.24 (s, 4H, H₇/H_{7'}), 7.54 (d, 4H, H₁₀/H_{10'}, *J* = 8 Hz), 7.94 (t, 2H, H₁₁/H_{11'}, *J* = 8 Hz). ¹³C NMR (DMSO-*d*₆, 400 MHz): δ = 162.29 (–CHO, DMF), 166.69 (C₁), 149.94 (C₂), 127.69 (C₃), 123.50 (C₄), 127.04 (C₅), 129.25 (C₆), 130.48 (C₇/C₁₁), 166.49 (C₈), 155.73 (C₉), 124.39 (C₁₀), 30.72 (CH_{3'}, DMF), 34.38 (CH_{3'}, DMF).}

Physical Methods. The FTIR spectra (KBr disk, 4000–400 cm⁻¹) were recorded with a Perkin-Elmer FTIR 2000 spectrometer. The conductivity measurements were carried out in organic solvents with a digital conductivity bridge from the Popular Traders, India (model no.: PT 825). The elemental analysis data were obtained with an Elementar Analysen Systeme GmbH Vario EL-III instrument. The NMR spectral measurements were carried out with a GEOL spectrometer (400 MHz) with TMS as the internal standard. The solution absorption spectra were recorded with a Perkin-Elmer Lambda-25 spectrophotometer.

Scheme 2. Preparative Routes for the Protected Complexes $3^{P}-6^{P}$ and Their Deprotected Complexes $3-8^{a}$



^aConditions: (a) K_2CO_3 , CH_2Cl_2 ; (b) $[Co(H_2O)_6](ClO_4)_2$; (c) $Et_4NCl\cdot xH_2O$ in O_2 atmosphere; (d) NaH, DMF, N_2 ; (e) $[Co(H_2O)_6](ClO_4)_2$; (f) excess O_2 ; (g) NaOH.



Figure 1. (a) Thermal ellipsoidal representation (30% probability level with partial numbering scheme) of complex 1; hydrogen atoms and solvent molecules are omitted for clarity. (b) H-bonding interactions between different synthons. (c) A view of packing diagram along the *c* axis.

The diffused reflectance spectra were recorded with a Perkin-Elmer Lambda-35 spectrophotometer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with DTG-60 Shimadzu and TA-DSC Q200 instruments, respectively, at a 5 °C min⁻¹ heating rate under nitrogen.

Crystallography. The intensity data for complexes 1, 2, 3, 4, and 6 were collected at 298 K, whereas for complexes 5, 7, and 8, the data were collected at 150 K on an Oxford XCalibur CCD diffractometer equipped with graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å).²² Data were processed with XCalibur S SAINT while the empirical absorption correction was applied using spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm.²² The structures were solved by the direct methods using SIR-97^{23a} and refined by the full-matrix least-squares refinement techniques on F^2 using the program SHELXL-97^{23b} incorporated in the WINGX 1.8.05 crystallographic collective package.^{35c} The hydrogen atoms were fixed at the calculated position with isotropic thermal parameters; however, the hydrogen atoms of the lattice water molecules (except O14W) and a hydronium ion for complex 5 were located from the difference Fourier map. The non-hydrogen atoms were refined anisotropically. However, the positionally disordered water molecule O14W (for complex 5) and hydronium ion

(O1W) and C12, C13, C14, N3, and O4 atoms of the DMF molecule (for complex 8) were refined isotropically. Complex 2 showed a positionally disordered water molecule O2W, and C40, Cl1, and Cl2 atoms of the dichloromethane molecule. These atoms were solved by using the PART command, and their positions were refined isotropically with the site occupancy factor (SOF) of O2WA (0.428) and O2WB (0.572), C40A (0.22) and C40B (0.78), Cl1A (0.22) and Cl1B (0.78), and Cl2A (0.22) and Cl2B (0.78). The oxygen atoms O3W (for complex 5), O2W (for complex 6), O1W (for complex 7), and O1W (for complex 8) were modeled as the hydronium ions. The hydronium ion was modeled based on its pyramidal geometry and its ability to accept one and donate three hydrogen bonds. The hydrogen atoms of the hydronium ion were located for complex 5, but not for the remaining complexes; however, the molecular formulas for all complexes include these hydrogen atoms. The poor crystal quality (R_{int} : ca. 11%) and the disorders associated with the lattice water molecules and hydronium ion were reflected in the high R values of complex 6. The solvent accessible voids (SAVs) were calculated using PLATON.^{23d} Details of the crystallographic data collection and structural solution parameters are provided in Table 1.



Figure 2. (a) Thermal ellipsoidal representation (30% probability level with partial numbering scheme) of complex 2; hydrogen atoms and solvent molecules are omitted for clarity. (b) H-bonding interactions between different synthons. (c) A view of packing diagram along the *c* axis.

	0		,	1		,		
bond ^a	1	2	3	4	5	6	7	8
Co1-N1 ^{i,iv,v(8)}	1.954(3)	1.960(3)	1.958(2)	1.953(2)	1.946(3)	1.989(8)	1.954(3)	1.949(3)
Co1-N2 ^{iv(8)}	1.960(3)	1.971(2)	1.861(2)	1.852(2)	1.852(3)	1.860(8)	1.850(3)	1.854(4)
Co1-N3	1.944(3)	1.923(3)	1.948(2)	1.960(2)	1.954(3)	1.957(8)	1.950(3)	
Co1-N4	1.925(3)	1.937(2)	1.979(2)	1.958(2)	1.951(3)	1.971(7)	1.955(3)	
Co1-N5	1.951(3)	1.940(3)	1.858(2)	1.847(2)	1.851(3)	1.868(8)	1.847(3)	
Co1-N6	1.951(3)	1.944(3)	1.969(2)	1.956(2)	1.951(3)	1.991(7)	1.956(3)	
^a Symmetry transforma	ations used to g	generate equivale	ent atoms for co	omplex 8: (i) –	x, -y, z; (iv) -	y, x, -z; (v) y,	-x, -z.	

Table 2. Selected Dond Lenguis A for Complexes 1–8 (Geometry around the Co 101)

RESULTS AND DISCUSSION

Synthesis and Characterization. Two types of Co^{3+} -based coordination complexes have been synthesized and studied in the present work. The first category has compounds 1 and 2, where bidentate ligands have been used and the general formula is $[Co^{3+}(Ligand)_3]$. The second class has complexes 3-8, where tridentate ligands are present with the general formula (cation) $[Co^{3+}(Ligand)_2]$. The bidentate ligands, HBL^{*p*-COOEt}

and HBL^{*m*-COOEt}, are the coupling products of pyridine-2-carboxylic acid with ethyl-4-amino benzoate or ethyl-3-amino benzoate, respectively. Similarly, the tridentate ligands, $H_2L^{p-COOMe}$ and $H_2L^{m-COOEt}$, were synthesized by coupling pyridine-2,6-dicarboxylic acid either with methyl-4-amino benzoate or with ethyl-3-amino benzoate, respectively. The complexes 1^P-6^P were synthesized by treating the deprotonated form of either bidentate or tridentate ligands with the Co(II) salt. The final Co(III) state was achieved

Crystal Growth & Design

Table 3. Selected	l Bond Ang	les [deg	for Comp	lexes 1–8 (Geometry	v around t	the Co ³⁺	Ion)
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bond ^a	1	2	3	4	5	6	7	8
⁽⁸⁾ v,iv,iN1-Co1-N2 ^{iv}	82.31(12)	82.34(11)	81.88(10)	81.84(9)	81.93(12)	80.1(3)	81.73(14)	81.94(9)
N1-Co1-N3	94.56(12)	87.87(11)	162.90(10)	163.77(10)	163.58(11)	161.8(3)	163.74(13)	
N1-Co1-N4	89.47(12)	94.57(11)	90.39(10)	90.36(9)	90.30(12)	92.2(3)	90.28(14)	
N1-Co1-N5	176.42(12)	96.21(11)	99.69(10)	98.63(9)	98.52(12)	95.1(3)	96.67(14)	
N1-Co1-N6	95.76(12)	176.27(11)	90.28(10)	91.57(9)	92.28(12)	90.8(3)	91.46(14)	
N2-Co1-N3	176.15(12)	95.01(11)	81.03(10)	81.93(9)	81.68(11)	81.7(3)	82.01(14)	
N2-Co1-N4	94.75(12)	176.54(11)	100.44(10)	98.77(9)	99.68(12)	103.4(3)	97.08(13)	
N2-Co1-N5	94.72(12)	86.20(11)	177.51(10)	179.13(9)	178.17(12)	173.5(3)	177.89(14)	
N2-Co1-N6	85.90(12)	93.98(10)	96.71(10)	97.47(9)	96.89(12)	95.0(3)	99.55(13)	
N3-Co1-N4	82.95(12)	83.29(11)	92.30(10)	92.11(9)	91.61(12)	90.6(3)	91.59(14)	
N3-Co1-N5	88.49(12)	175.87(11)	97.41(10)	97.60(9)	97.89(12)	103.1(3)	99.58(14)	
N3-Co1-N6	96.67(12)	93.06(11)	92.10(10)	90.52(9)	90.53(12)	92.2(3)	91.35(14)	
N4-Co1-N5	92.78(12)	95.72(11)	81.53(10)	81.97(9)	82.11(12)	81.1(3)	81.54(13)	
N4-Co1-N6	174.77(12)	89.13(11)	162.76(10)	163.76(10)	163.43(11)	161.6(3)	163.36(13)	
N5-Co1-N6	81.99(11)	82.91(11)	81.38(10)	81.79(9)	81.33(12)	80.6(3)	81.83(13)	
^a Symmetry transformatio	ons used to gene	erate equivalent	atoms for comp	olex 8: (i) -x, -	-y, z; (iv) $-y, x$	-z; (v) y, -	x, -z.	

Table 4	Selected	H-Bond	Parameters	for	Complexes	1	and 2
I able 4.	Selected	11-Dullu	r al ameters	101	Complexes	1	anu 2

complex	$D-H\cdots A^{a}$	$d(H \cdots A)$ (Å)	$d(D \cdots A)$ (Å)	∠(DHA) (deg)
1	O5–H5A····O2 ⁱ	1.88	2.700(2)	174
	O7–H7A···O3 ⁱⁱ	1.80	2.589(3)	161
	O9–H9A…O2 ⁱⁱⁱ	1.88	2.701(4)	174
2	O5–H5A…O1 ⁱ	1.91	2.681(5)	156
	O7–H7A····O6 ⁱⁱ	1.83	2.648(4)	178
	09–H9A…O3 ⁱⁱⁱ	1.85	2.649(5)	164

^aSymmetry transformations used to generate equivalent atoms for complex 1: (i) 1/2 - x, 1/2 + y, 1/2 - z; (ii) 3/2 - x, 1/2 + y, 1/2 - z; (iii) 1/2 - x, -x, -1/2 + y, 1/2 - z; for complex 2: (i) 1 - x, 1 - y, 1 - z; (ii) 2 - x, -y, -z; (iii) 1 - x, -y, -z.

through dioxygen-mediated oxidation. The complexes $1^{P}-6^{P}$ contain protected carboxylic acids groups at the periphery. The subsequent deprotection using base-assisted hydrolysis afforded the final complexes 1-8 with free carboxylic acid groups at the periphery (Schemes 1 and 2). The complexes 1, 2, and 3-8 were isolated as brick-red and deep green crystalline solids, respectively, after recrystallization. Complexes 1 and 2 are neutral in nature as the 3+ charge on the Co(III) ion is balanced by three monoanionic bidentate ligands. On the other hand, the remaining complexes with tridentate ligands are monoanionic in nature. In the cases of complexes 3 and 4, Et_4N^+ balances the charge, whereas in complexes 5-8, the charge is balanced by the protonated form of the water molecule (i.e., hydronium ion, H_3O^+). The evidence for the presence of H₃O⁺ has come from the conductivity measurements²⁴ that show a 1:1 electrolytic nature for complexes 5-8 as well as an acidic nature of their aqueous and/or methanolic solution. The protonation has most probably occurred during the deprotection step where excess NaOH was neutralized by the addition of HCl.

The deprotected complexes 1-8 show broad signals between 3402 and 3427 cm⁻¹, which have been assigned to ν_{O-H} due to both free carboxylic acid (-COOH) and water molecules that are present in the lattice (Table S1, Supporting Information).²⁵ Importantly, such -COOH stretches were absent in their precursor complexes (1^P-6^P) with the protected carboxylic acid groups. The signals between 1702 and 1718 cm⁻¹ correspond to the ν_{COO} of free carboxylate groups, whereas protected complexes, 1^P-6^P , show these stretches at slightly higher values. In addition, the proton NMR spectra display a broad feature between 11 and 12 ppm for the presence of free -COOH groups, which disappeared on the addition of D₂O.

The D₂O-exchange experiments strongly support the presence of free carboxylic acid groups in the deprotected complexes. All complexes show well-resolved signals in their proton as well as carbon NMR spectra, and these techniques are the simplest method to characterize the present complexes (Figures S1–S18, Supporting Information). The absorption spectra for all cobalt complexes were studied in CH₃OH, and the λ_{max} were observed within the range of 625–650 nm (Figures S19–S24, Supporting Information). The observed feature is due to the d–d transition of the Co(III) ion. The high-energy features were observed below 350 nm and could tentatively be assigned to intraligand transitions.

Thermal Studies. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis were performed on all complexes to study the thermal stability of the hydrogenbonded networks and the fate of lattice solvent molecules (Figures S25–S32, Supporting Information). Typically, the loss of lattice water molecules was observed in the temperature range of 20-100 °C, whereas complexes 7 and 8 show the loss of DMF at relatively higher temperature (between 140 and 180 °C). For complex 1, the observed weight loss (11.37%) fits nicely with the calculated value of 11.04% for the loss of five water molecules. For complex 2, the weight loss (obs, 8.76%; calcd, 9.47%) corresponds to the loss of one CH_2Cl_2 molecule. For complex 3, the weight loss (obs, 9.65%; calcd, 9.60%) is related to the loss of six water molecules. A weight loss between 28 and 170 °C (obs, 14.69%; calcd, 14.86%) corresponds to the loss of one water and one Et_4N^+ cation for complex 4. The TG curve of 5 shows the weight loss (obs, 18.60%; calcd, 18.50%) for the loss of 10 water molecules and 1 hydronium ion. For 6, the weight loss (obs, 10.74%; calcd, 9.94%) corresponded to the loss of four water molecules and one hydronium ion. In a similar manner, complex 7 shows the weight loss (obs, 11.03%; calcd, 10.97%) for the loss of one





Figure 3. (a) Thermal ellipsoidal representation (30% probability level with partial numbering scheme) of complex 3; hydrogen atoms, cation, and solvent molecules are omitted for clarity. (b) Figure showing H-bonding interactions involving water molecules (shown in red color). (c) A view of packing diagram along the *c* axis. (d) A portion of the network showing the presence of Et_4N^+ cations (space-filling mode) within the void.

water, one hydronium ion, and one DMF molecule. Similarly, complex 8 shows the weight loss (obs, 11.07%; calcd, 11.43%) for the loss of two water molecules, one hydronium ion, and one DMF. All complexes show the second weight loss above 270 °C, which corresponds to the decomposition of the framework. In DSC analysis, complexes 1-6 show exothermic features between 20 and 140 °C for the loss of lattice water molecules. On the other hand, complexes 7 and 8 display a broad feature for the loss of a DMF molecule in the exothermic region of 140-180 °C. In most cases, a nice match was observed between the thermal weight loss to that of crystallographically observed lattice solvent molecules as well as microanalysis results (cf. Table S2, Supporting Information).

Crystallography. All deprotected cobalt(III) compounds have been characterized by the single-crystal X-ray diffraction analysis to understand their molecular structures, orientation of the appended arylcarboxylic acid groups, and H-bond-based self-assembly. The relevant crystallographic data and structure solution parameters are summarized in Table 1, whereas the selected bond lengths and bond angles are given in Tables 2 and 3. The H-bonding geometries are listed in Tables 4–7.

Crystal Structures of Complexes 1 and 2. Complexes 1 and 2 crystallized in monoclinic $(P2_1/n \text{ space group})$ and triclinic cell systems ($P\overline{1}$ space group), respectively. The molecular structures and self-assemblies of complexes 1 and 2 are shown in Figures 1 and 2, respectively. Three bidentate pyridine-amide ligands appended with either *p*- or *m*-arylcarboxylic acid groups are arranged octahedrally around the Co³⁺ ion (Figures 1a and 2a). The ligands coordinate the Co³⁺ ion via a five-membered chelate ring between amide-*N* and pyridyl-*N* atoms. The Co–N_{amide} bond distances (avg 1.949 Å) are comparable to Co–N_{pyridine} bond distances (avg. 1.939 Å), suggesting a symmetrical bonding from all donors (Table 2).^{20a} All diagonal angles are more or less linear in nature, ranging from 174.8° to 176.4°, again suggesting a symmetrical arrangement of donors, resulting in a nearly



4c

4d



Figure 4. (a) Thermal ellipsoidal representation (30% probability level with partial numbering scheme) of complex 4; cation and hydrogen atoms are omitted for clarity. (b) A portion of the network showing intermolecular H-bonding between different molecules. (c) Space-filling model of the packing diagram. (d) A portion of the network showing the presence of Et_4N^+ cations (space-filling mode) within the void.

Table 5. Selected H-B	ond Parameters for	Complexes 3 and 4
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complex	$D-H\cdots A^{a}$	$d(H \cdots A)$ (Å)	$d(D \cdots A)$ (Å)	∠(DHA) (deg)
3	O5–H5A…O2W ⁱ	1.85	2.656(5)	169
	O7–H7A····O3W ⁱⁱ	1.67(6)	2.595(5)	168(4)
	O9–H9A…O4W ⁱⁱⁱ	1.83(7)	2.724(5)	175(7)
	O11-H11A····O7W ^{iv}	1.61(8)	2.592(5)	163(7)
4	O5–H5A····O2 ⁱ	1.80(5)	2.668(4)	159(4)
	O7–H7A…O1 ⁱⁱ	1.71(3)	2.631(3)	160(3)
	09–H9A…O4 ^{ііі}	1.76(4)	2.629(3)	160(3)
	O11-H11AO3 ^{iv}	1.75(5)	2.584(3)	172(4)

^aSymmetry transformations used to generate equivalent atoms for complex 3: (i) 2 - x, 1 - y, 1 - z; (ii) 1 + x, -1 + y, z; (iii) -x, 1 - y, 1 - z; (iv) -x, 1 - y, -z; for complex 4: (i) -1/2 + x, 1/2 - y, -1/2 + z; (ii) 1/2 + x, 1/2 - y, 1/2 + z; (iv) 1/2 + x, 1/2 - y, -1/2 + z; (iv) 1/2 + x, 1/2 - y, 1/2 + z; (iv) 1/2 + x, 1/2 - y, -1/2 + z; (iv) 1/2 + x, 1/2 - y, 1/2 + z; (iv) 1/2 + x, 1/2 - y, -1/2 + z; (iv) 1/2 + x, 1/2 - y, 1/2 + z; (iv) 1/2 + x, 1/2 - y, -1/2 + z; (iv) 1/2 + x, 1/2 - y, 1/2 + z; (iv) 1/2 + x, 1/2 - y, -1/2 + z; (iv) 1/2 + x, 1/2 - y, 1/2 + z; (iv) 1/2 + x, 1/2 - y, -1/2 + z; (iv) 1/2 + x, -1/2 + z; (iv) 1/2 + x, -1/2 + z; (iv) 1/2 + x; (iv)

octahedral geometry (Table 3). Notably, significant reduction of the bond angles from 90° involving the five-membered chelate rings was observed. Such an observation indicates a tight chelation; in fact, the average angle is only \sim 83°. In both 1 and 2, the crystal structures clearly illustrate the *meridional* (*mer*) geometric form at the metal, as the dihedral angle between the coordinating planes comprising either three amide-*N* atoms or three pyridyl-*N* atoms is close to 180°. The occurrence of the *mer* form has made all three associated ligands asymmetrical to each other, and this ligand asymmetry was observed in IR and ¹H NMR spectra with 3-fold signals.^{20a,26a} In both 1 and 2, the presence of the *mer* form is quite unique and interesting, which places the three appended arylcarboxylic acid groups to different directions. Such a situation is in complete contrast to the cases where three bidentate ligands are arranged in *facial* (*fac*) form and the appended groups are projected in a nearly *C*₃ symmetric fashion.^{27,28}



Figure 5. (a) Thermal ellipsoidal representation (30% probability level with partial numbering scheme) of complex 5; hydrogen atoms, cation, and solvent molecules are omitted for clarity. (b) A portion of the network showing H-bonding between molecular components. (c) A view of packing diagram along the *a* axis. (d) A space-filling representation of the network in a view along the *a* axis; water molecules are shown in red color.

Notably, both complexes 1 and 2 are appended with the arylcarboxylic acid groups. A –COOH group is unique as it is capable of functioning both as H-bond donor (through H atom) as well as acceptor (through O atom). In addition, both complexes 1 and 2 also have O_{amide} groups that can act as the H-bond acceptors. Thus, a combination of H-bond donors (H_{acid}) and H-bond acceptors (O_{amide} and O_{acid}) is being offered. As a consequence, both complexes self-assemble into complementary supramolecular networks via intermolecular H-bonding between –COOH and O_{amide} groups

(Table 4). In addition, complex **2** also shows conventional intermolecular H-bonding between H_{acid} and O_{acid} groups, resulting in the generation of the [COOH]₂ dimer.^{14b} For **1**, the carboxylic O–H groups O5–H5A, O7–H7A and O9–H9A interact with the complementary O_{amide} groups O2, O3, and O2[#], forming O5–H5A···O2ⁱ, O7–H7A···O3ⁱⁱ, and O9–H9A···O2ⁱⁱⁱ motifs (Figures 1b and 1c). The heteroatom separations between the interacting groups were found to be between 2.589(3) and 2.701(4) Å, while the O–H···O_{amide} angles were between 161 and 174°.



6c

6d



Figure 6. (a) Thermal ellipsoidal representation (30% probability level with partial numbering scheme) of complex **6**; hydrogen atoms, cation, and solvent molecules are omitted for clarity. (b) A view showing the H-bonding between carboxylic acids, lattice water molecules, and hydronium ions. (c) A view of packing diagram along the *a* axis. (d) A space-filling representation of the network in a view along the *a* axis; water molecules and hydronium ions are shown in red and blue color, respectively.

These $O-H_{acid}\cdots O_{amide}$ interactions led to the generation of 1D chains. These chains are further connected to each other via $O-H_{acid}\cdots O_{amide}$ H-bonding interactions to generate the 2D network. There are additional H-bonding involving O_{acid} atoms O4 and O6 to that of lattice water molecules O1W and O2W (O4…O2W: 3.032 Å and O6…O1W: 2.789 Å), which strengthens the network.

Similarly, in complex **2**, the carboxylic O–H groups (O5– H5A and O9–H9A) interact with the complementary O_{amide} atoms O1 and O3, forming the O5–H5A···O1ⁱ and O9–H9A···O3ⁱⁱⁱ motifs (Figure 2b,c). The heteroatom separations and O–H···O_{amide} angles were found to be 2.681(5) and 2.649(5) Å, and 156 and 164°, respectively. The carboxylic acid O–H group (O7–H7A) further interacts with the O_{acid} (O7–H7A···O6ⁱⁱ: 2.648(4) Å) to generate a [COOH]₂ cyclic dimer^{14b} that results in the formation of a 2D network. The D–H···A bond angle for the [COOH]₂ cyclic dimer was found to be 178°, which is very close to the ideal angle of 180° for an isolated dimer.^{14b} The crystal structure of complex **1** shows solvent accessible voids (SAVs) with a volume of 1130 Å³, which is ca. 25% of the unit cell volume (4462 Å³). Interestingly, complex **2** does not offer any considerable void, and we believe that a highly complementary interaction between the interacting groups has prevented the generation of void space.

Crystal Structures of Complexes 3 and 4. Complexes 3 and 4 were found to crystallize in triclinic ($P\overline{1}$ space group) and monoclinic cell systems ($P2_1/n$ space group), respectively. Both of these complexes are anionic in nature, and the charge is being balanced by the Et_4N^+ cation. The molecular structures of 3 and 4 are quite similar and show that the central Co^{3+} ion is meridionally coordinated by two tridentate pyridine-amide based ligands (Figures 3a and 4a).^{20a,26} The octahedral Co^{3+} ion is coordinated to four anionic N_{amide} atoms in the basal plane and two $N_{pyridine}$ distances were found to be in the ranges of 1.948(2)–1.979(2) and 1.847(2)– 1.861(2) Å, respectively (Table 2). In both cases, axial pyridine rings are trans to each other and make an angle in excess of 177°. The diagonal N_{amide} groups make angles of nearly 163° with the central Co^{3+} ion in both cases (Table 3). The bonding parameters for

Table 6. Selected H-Bond Parameters for Complexes 5 and 6

complex	$D-H\cdots A^{a}$	$d(H \cdots A)$ (Å)	$d(D \cdots A)$ (Å)	∠(DHA) (deg)
5	O1W–H1A…O3 ⁱ	1.82	2.645(4)	163
	O2W–H2A···· O1 ⁱⁱ	1.79	2.705(4)	157
	O3W-H3A…O1	2.05	2.871(4)	158
	O3W-H3B…O12	2.08	3.001(5)	157
	O4W-H4A····O4 ⁱⁱ	1.91	2.789(4)	165
	O5–H5A····O6W ⁱⁱⁱ	1.78	2.607(4)	166
	O6W–H6A····O2 ^{iv}	2.10	2.993(4)	156
	O6W–H6B…O8 ^v	1.85	2.787(5)	158
	O7–H7A····O5W ^{vi}	1.74	2.561(5)	165
	O8W–H8A…O6 ^{vii}	2.15	2.982(5)	142
	O8W-H8B····O3	1.90	2.814(6)	156
	O9-H9A····O10W ^{viii}	1.82	2.616(6)	158
	O10W-H10A····O10 ^{ix}	1.79	2.600(6)	149
	O10W-H10B…O12	2.08	2.828(5)	131
	O11–H11A…O4W ^x	1.76	2.578(5)	165
	O5W-H55B…O6	2.04	2.902(5)	159
	O7W-H77AO2	1.94	2.755(6)	167
	O9W-H99BO4	1.89	2.819(5)	156
	O11W-H111…O6	1.98	2.808(6)	147
6	O1W-H1B…O1 ⁱⁱ	1.86(15)	2.537(14)	153(17)
	O5–H5A····O3 ⁱⁱⁱ	1.90	2.658(14)	153
	O7–H7A····O2W	1.81	2.62(2)	171
	O9–H9A…O10 ^{iv}	1.85	2.669(17)	173
	O11–H11A…O2 ^v	1.86	2.630(11)	157
				<i>/ / / / / / / / / /</i>

^aSymmetry transformations used to generate equivalent atoms for complex 5: (i) 1 - x, -y, 1 - z; (ii) 1 - x, 1 - y, 1 - z; (iii) 1 + x, y, z; (iv) x, y, 1 + z; (v) -1 + x, y, 1 + z; (vi) 2 - x, 1 - y, -z; (vii) -1 + x, y, z; (viii) -x, -y, -z; (ix) x, 1 + y, z; (x) -x, 1 - y, 1 - z; for complex 6: (ii) -1 + x, -1 + y, z; (iii) 2 - x, 1 - y, -z; (iv) 2 - x, 1 - y, 1 - z; (v) 1 - x, 2 - y, 1 - z.

complexes 3 and 4 are in line with our earlier systems as well as to that of literature examples with similar ligands. 20a,26

These molecules are appended with four peripheral H-bonding donor -COOH groups and have the ability to selfassemble, considering the fact that there are H-bonding acceptors in O_{acid} and O_{amide} groups (Table 5). For complex 3, the -COOH groups act as H-bond donors, while the lattice water molecules function as acceptors, although C=O_{amide} groups are also present. In this case, for every -COOH group, two water molecules were present in the crystal lattice and found to be significantly involved in H-bonding with the -COOH groups. The carboxylic acid O-H groups interact with the lattice water molecules, forming the O5-H5A···O2W, O7-H7A···O3W, O9-H9A···O4W, and O11-H11A···O7W motifs, respectively (Figure 3b,c). The heteroatom separations and the $O-H_{acid}$... O_{water} angles were found to be between 2.592(5) and 2.724(5) Å and in excess of 163°, respectively. Interestingly, because of the presence of lattice water molecules, the carboxylic acid O-H groups were not interacting at all with the C=O_{amide} groups, a feature that has been typically observed in the remaining systems. The lattice water molecules are arranged in the form of an octagon within the H-bonded network. Complex 3 does not offer adequate SAVs as the void space is filled with the lattice water molecules and Et_4N^+ cations, as shown in Figure 3d.

In the case of complex 4, the -COOH groups that are appended at the *meta* position have resulted in a highly symmetrical and interesting self-assembly. Each building block shows H-bonding interaction with four neighboring building blocks, and the extension of such interactions generates a 2D sheet (Figure 4b,c). Importantly, no water molecule was found in the crystal lattice of complex 4, thus minimizing the competition from the water molecules, as noted in complex 3. The carboxylic acid O–H groups were found to interact symmetrically with the complementary O_{amide} atoms, forming the O5–H5A···O2ⁱ, O7– H7A···O1ⁱⁱ, O9–H9A···O4ⁱⁱⁱ, and O11–H11A···O3^{iv} motifs, respectively. For these motifs, the heteroatom separations between 2.584(3) and 2.668(4) Å and O–H···O_{amide} angles between 159 and 172° were observed. A highly symmetrical array of H-bonds between H_{acid} and O_{amide} groups has prevented these functional groups from further interacting with other atoms/groups. As an example, even highly stable intermolecular H-bonded [COOH]₂ dimers were not formed.¹⁴ Complex 4 showed very small SAVs of 214 Å³ (only ca. 4% of the unit cell volume), which were almost fully occupied by the Et₄N⁺ cations (Figure 4d).

Crystal Structures of Complexes 5 and 6. Both complexes 5 and 6 crystallized in a triclinic cell system with the $P\overline{1}$ space group. In both compounds, the negative charge on the complex anion was balanced by the presence of a hydronium ion (H_3O^+) . The Co³⁺ ion has octahedral geometry where the basal plane is composed of N_{amide} groups while the axial positions are occupied by the N_{pyridine} atoms (Figures 5a and 6a).^{20a,26} The Co–N_{amide} and Co–N_{pyridine} distances were found to be in the ranges of 1.946(3)–1.991(7) and 1.851(3)–1.868(8) Å, respectively (Tables 2 and 3).

Notably, there were 13 lattice water molecules and $1 H_3O^+$ in complex **5**, whereas only 2 water molecules and a hydronium ion were present in complex **6**. In both **5** and **6**, the hydronium ion plays a very important role. It not only balances the charge but also shows interesting H-bonding interactions with the carboxylic acid O–H groups, O_{amide} atoms, and lattice water molecules (Table 6). In **5**, the H_{acid} groups O5–H5A, O7–H7A, O9–H9A, and O11–H11A were interacting with the hydronium ion O3W, and water molecules O6W, O5W, O10W, and O4W, respectively (Figure Sb). The resultant O5–H5A···O6Wⁱⁱⁱ,



Figure 7. (a) Thermal ellipsoidal representation (30% probability level with partial numbering scheme) of complex 7; hydrogen atoms, cation, and solvent molecules are omitted for clarity. (b) A view showing the H-bonding between carboxylic acids, lattice water molecules, and hydronium ions. (c) Packing diagram in a view along the *a* axis. (d) Packing diagram (space-filling mode) in a view along the *c* axis; water molecules and hydronium ions are shown in red and blue color, respectively.

 $O7-H7A\cdots O5W^{vi}$, $O9-H9A\cdots O10W^{iii}$, and $O11-H11A\cdots O4W^{x}$ motifs have the heteroatom separations between 2.561 and 2.616 Å, while the $O-H\cdots O_{water}$ angle was within $158-165^{\circ}$ (Table 6). These interactions resulted in the generation of a chain running along the *a* axis (shown in magenta color; Figure 5c). One such chain further connects to other parallel running chains in the same direction (shown in pink color; Figure 5c) through the hydronium ion as well as lattice water molecules (shown as red color ball; Figure 5c). These interactions led to the generation of a closely packed 2D network that does not show any SAVs (Figure 5d).

In the case of complex **6**, the carboxylic O–H groups O5– H5A, O7–H7A, O9–H9A, and O11–H11A interact with the O_{amide}, O_{carboxylate}, and hydronium ion (O3, O2W, O10, and O2, respectively) (Figure 6b,c). The O5–H5A···O3ⁱⁱⁱ, O7– H7A···O2W, O9–H9A···O10^{iv}, and O11–H11A···O2^v motifs have the heteroatom separations between 2.620(2) and 2.669(17) Å (Table 6). The average O-H…O_{amide} and $O{-}H{\cdots}O_{water}$ bond angles were found to be ca. 161° and ca. 171°, respectively. These interactions resulted in the generation of a chain running along the *a* axis (shown in yellow color; Figure 6c). A yellow chain further connects with the parallel running chains in the same direction (shown in pink color; Figure 6c) through the formation of the $[\mbox{COOH}]_2$ dimer between $H_{\mbox{acid}}$ and O_{carboxylate} groups as well as via the hydronium ion. For the [COOH]₂ dimer, the O-H…O bond angle of 173° and separation of 2.669(17) Å were noted.^{14b} The lattice water molecules (shown as red color ball; Figure 6c) do not play any significant role in the connection of two chains and only interact with the O_{amide} atoms (Figure 6c). The crystal structure of complex 6 showed a very small SAV of 61 ${\rm \AA}^3$ (2.5% of the unit cell volume), which is partially occupied by the hydronium ion and lattice water molecules (Figure 6d).



Figure 8. (a) Thermal ellipsoidal representation (30% probability level with partial numbering scheme) of complex 8; hydrogen atoms, cation, and solvent molecules are omitted for clarity. (b, c) A portion of the network showing intermolecular H-bonding between different molecules. (d) A view of packing diagram (space-filling mode) along the *c* axis.

Table 7. Selecte	d H-Bond	Parameters	for C	omplexes	7	and	8
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complex	$D-H\cdots A^{a}$	$d(H \cdots A)$ (Å)	$d(D \cdots A)$ (Å)	∠(DHA) (deg)
7	05–H5A…013 ⁱ	1.79	2.629(6)	174
	O7–H7A····O1 ⁱⁱ	1.78	2.609(6)	170
	09–H9А…ОЗ ^{ііі}	1.75	2.505(6)	148
	011–H11A…O9 ^{iv}	1.91	2.726(5)	163
8	O3–H3A…O1 ⁱ	1.81	2.599(5)	157
^a Symmetry transformation	s used to generate equivalent ator	ms for complex 7: (i) $2 - x$, 2	-y, 1-z; (ii) $x, -1+y, z;$	(iii) $-x$, $2 - y$, $1 - z$; (iv) $-x$

2 - y, -z; for complex 8: (i) 1/2 + y, -1/2 + x, 1/2 + z.

Crystal Structures of Complexes **7** *and* **8**. Complex 7 crystallized in a triclinic cell system with the $P\overline{1}$ space group, whereas complex 8 crystallized in a tetragonal cell system with the $P42_1c$ space group. As noted for complexes **5** and **6**, in both 7 and **8**, the negative charge on the complex anion is balanced by the hydronium ion (H_3O^+) . In each case, the octahedral Co^{3+} ion is surrounded in a N₆ donor environment (Figures 7a and 8a). The Co–N_{amide} and Co–N_{pyridine} distances were found to be in

the ranges of 1.950(3)–1.956(3) and 1.847(3)–1.861(5) Å, respectively (Tables 2 and 3). 20a,26

Complex 7 was recrystallized from DMF, and as a result, one DMF was found to co-crystallize in the lattice that was actively participating in the H-bonding. In 7, the H_{acid} groups O5–H5A, O7–H7A, O9–H9A, and O11–H11A interact with O_{DMF}, O_{amide}, and O_{carboxylates} atoms (Figure 7b). The O5–H5A···O13ⁱ, O7–H7A···O1ⁱⁱ, O9–H9A···O3ⁱⁱⁱ, and O11–H11A···O9^{iv} motifs

have the heteroatom separations between 2.505(6) and 2.726(5) Å while the O–H···O_{donor} angles were within $163-174^{\circ}$ (Table 7). These interactions resulted in the generation of a double chain running along the *a* axis (shown in pink color; Figure 7c). One such double chain further connects with the neighboring chains through the lattice water molecules (shown in red color), hydronium ions (shown in blue color), and DMF molecules (shown in gray color, Figure 7c). All such interactions resulted in a 2D sheetlike architecture. The structure of complex 7 showed SAVs of 453 Å³ in volume (18% of the unit cell volume of 2548 Å³) and cavities of 14×12 Å², which are occupied by DMF, hydronium ions, and lattice water molecules (Figure 7d).

Complex 8 shows a highly symmetrical and complementary H-bonding where every building block was found to interact with four neighboring molecules (Figure 8b,c). Here, the H_{acid} group O3–H3A interacts with the complementary O_{amide} atom O1, forming the O3–H3A···O1ⁱ motif with the heteroatom separation of 2.597(7) Å and O–H···O_{amide} angle of 155° (Table 7). Such interactions resulted in the creation of a chain running along the *c* axis (shown in violet color; Figure 8d). Further, one such chain was found to be connected with the other parallel running chain (shown in pink color) via O–H···O_{amide} synthons. Because of a symmetrical and highly complementary H-bonding interaction, complex 8 does not offer any void space (Figure 8d). Furthermore, the symmetrical nature of H-bonding deprives the hydronium ion of interacting with other functional groups, and it remains isolated within the lattice.

SALIENT FEATURES AND CONCLUSIONS

There are a number of structural features that categorically distinguish two sets of complexes, that is, complexes with parylcarboxylic acid appended groups to that of *m*-arylcarboxylic acid appended groups. For example, the numbers of cocrystallized water molecules were found to be much higher in the case of complexes with *p*-arylcarboxylic acid appended groups than that of meta analogues. Therefore, in complexes with p-arylcarboxylic appended groups, the H-bonding always took place through the lattice water molecules. Thus, water molecules functioned as the "spacers" and elongated the H-bonded network.¹⁹ In complete contrast, complexes with *m*-arylcarboxylic acid appended groups self-assembled through complementary H_{acid} ...O_{amide} synthons. As a consequence of highly symmetrical and complementary H-bonding, the complexes with *m*-arylcarboxylic appended groups either offered small SAVs or did not offer at all. In essence, because of the closely packed network in meta cases, the solvent molecules did not cocrystallize in large numbers. However, in cases of para analogues, a loosely packed network (due to not so highly symmetrical H-bonding) offered voids that could be occupied by the solvent molecules. Thus, the symmetrical versus not highly symmetrical nature of self-assembly in para versus meta systems dictates the fate of co-crystallized solvent molecules and packing behavior. Notably, the typically stable and frequently observed [COOH], dimer has only been noted in two cases: complexes 2 and 6; both of them have *m*-arylcarboxylic acid appended groups.

The type of cation present also influenced the outcome of the network generation. For example, whenever a hydronium ion was present in the lattice, it actively participated in the H-bonding and helped in the elongation of the network in conjunction with additional H-bonding synthons. However, in cases where the Et_4N^+ cation was present, it did not effectively participate in the weak interactions and rather remained as an isolated entity within the H-bonded network and occupied the voids (see Figures 3d and 4d, for example).

Finally, the type(s) of lattice solvent molecules (water vs DMF) also affected the network generation. For example, the presence of DMF in complex 7 showed that it not only actively participated in the H-bonding but also complemented the lattice water molecules in the network creation. For complex 8, analytical data and diffraction studies established the presence of DMF in the lattice. However, the highly disordered nature of this DMF molecule has restricted us in evaluating its role in the H-bonding network.

It is opined that the coordination complexes appended with Hbond-sensitive functional groups provide a far more challenging situation to study the H-bonded structures as a coordination complex significantly influences the placement of the functional group and generates unconventional geometrical motifs.^{14,27,28} Our ongoing work is exploring placing the appended carboxylic acid groups at multiple position(s) on the arene ring to further increase the number of carboxylic acid groups per building block to evaluate their role in the H-bonding-based network creation.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for complexes 1-8 in CIF format, NMR spectra (Figures S1–S18), absorption spectra (Figures S19–S24), TGA-DSC plots (Figures S25–S32), and tables. This material is available free of charge via the Internet at http://pubs. acs.org.

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Notes

The authors declare no competing financial interest.

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