

Co³⁺-Based Building Blocks with Appended Phenol and Catechol Groups: Examples of Placing Hydrogen-Bond Donors and Acceptors in a Single Molecule

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Supporting Information



ABSTRACT: This work shows the syntheses, structures, and hydrogen-bonding based self-assembly of Co^{3+} coordination complexes containing appended phenol and catechol groups. Placement of hydrogen-bond donors (in O–H groups of phenol and catechol) and acceptors (in C=O_{amide} groups) in a single molecule results in a complementary yet unique self-assembly.

INTRODUCTION

The rational design of molecular solids has attracted considerable interest in the area of designed and functional materials.^{1,2} Such solids hold promise as microporous materials with applications in gas storage, separation, sensing, and catalysis.^{3,4} A good number of examples are available utilizing the concept of spontaneous self-assembly. Such a self-assembly has been achieved taking advantage of either metal-ligand coordinate bond formation^{3a,b} or weak but directional interactions, such as hydrogen bonding (H-bonding).⁵ The hydrogen bond (H-bond), an important noncovalent interaction with directionality and moderate bond strength, is a valuable tool in crystal engineering.⁵ Phenol and phenolic group-based building blocks are known to afford a variety of supramolecular networks.⁶ The stability and the utility of these networks depend on both the quality and the quantity of such interactions that constitute the resultant supramolecular architecture. Multiple intermolecular interactions between participating molecules give rise to cooperative stabilization of the final architecture. In this category, considerable work has been done with bis-, tris-, tetrakis-, and multikis-phenols to understand their self-assembly process.⁶ Notably, these phenolbased synthons are known to afford a variety of supramolecular networks, where the phenolic group plays a crucial role in the formation of characteristic H-bonded motifs.⁷ Noteworthy are the examples from the groups of Desiraju,⁸ Wuest,⁹ Toda,¹⁰

Nangia,¹¹ Suslick,¹² Baruah,¹³ Aoyama and Kobayashi,¹⁴ and others.¹⁵ In particular, Tominaga et al.¹⁶ have shown the generation of predictable networks due to the mechanically robust and conformationally well-defined nature of a few adamantane-based phenol derivatives in conjunction with cooperative interactions.

Our research has been focusing on developing coordination complexes as the building blocks for the construction of ordered structures.¹⁷ A coordination complex as the building block offers structural rigidity, and such an induced rigidity has the ability to place the auxiliary functional groups into 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 synthetic strategy has allowed us to prepare the $\{M^{n+}-Co^{3+}-M^{n+}\}$ heterobimetallic complexes $(M^{n+} = Zn^{2+}, Cd^{2+}, Hg^{2+}, and Cu^+)^{17a-c}$ and $\{Co^{3+}-Zn^{2+}\}^{17e}$ or $\{Co^{3+}-Cd^{2+}\}^{17f}$ networks of a highly ordered nature (Scheme 1). In the aforementioned systems, selection of the secondary metal was targeted to harness the Lewis acidic property in catalysis and that was indeed shown by several organic transformations.^{17,18} The second strategy was to introduce H-bond based functional

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Scheme 1. Pyridine-Based Building Blocks and Their Zero-Dimensional Hetero-Bimetallic Complexes and Two-Dimensional Networks (A Schematic Representation Only)



Scheme 2. Phenol and Catechol-Based Building Blocks 1-3 Discussed in This Work



groups that have the propensity to self-assemble, and we chose phenol and catechol groups for that purpose. The present work explores the self-assembly of Co^{3+} -based building blocks appended with phenol and catechol groups. An important aspect of this work is that the titled complexes offer both Hbond donors (in O–H group) as well as acceptors (in O= C_{amide} group) in a single molecule (Scheme 2). Thus, these functional groups are expected to operate in a highly complementary manner where the O–H groups will function as the H-bond donors and the O_{amide} groups will act as the complementary H-bond acceptors. Interestingly, the systematic presence and/or absence of such complementary functional groups may help in understanding the rational design of the resultant supramolecular architecture.

In particular, we have designed complexes $[Co(L^{p-OH})_2]^-(1)$ and $[Co(L^{m-OH})_2]^-(2)$ (where H_2L^{p-OH} : N,N'-bis(4hydroxyphenyl)pyridine-2,6-dicarboxamide) and H_2L^{m-OH} : N,N'-bis(3-hydroxyphenyl)pyridine-2,6-dicarboxamide) which differ by the systematic placement of an -OH group at the para or meta position of the arene ring, respectively. Further, if two rings containing p- and m-phenol are merged together, it would give rise to a catechol ring. Thus, a catechol-based complex $[Co(L^{cat})_2]^-(3)$ (where H_2L^{cat} : N,N'-bis(3,4dihydroxyphenyl)pyridine-2,6-dicarboxamide) was also designed to systematically understand the network creation due to the H-bond donors and H-bond acceptors. Of course, the catechol-based molecule 3 has more numbers of H-bond donors than acceptors, and it would be interesting to see the effect of this mismatch on the self-assembly (Scheme 2).

EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, chemicals and reagents were obtained from commercial sources and used without further purification. Prior to use, solvents were purified following the standard procedures.¹⁹

Syntheses of Ligands. 2,6-Bis(4-methoxy-benzene-carbamoyl)pyridine (H_2L^{p-OMe}) . To a solution of pyridine-2,6dicarboxylic acid (2.0 g, 0.011 mol) in pyridine (20 mL) was added 4-methoxy aniline (2.94 g, 0.023 mol) and triphenylphosphite (7.4 g, 0.023 mol) while stirring. The resulting mixture was stirred at 110 °C for 6 h. After the solution was cooled, excess pyridine was removed under reduced pressure. The resulting thick oil was dissolved in dichloromethane (50 mL), and the product was extracted in aqueous hydrochloric acid (150 mL, 1:1 v/v). The acidic aqueous extract was neutralized by the addition of solid sodium bicarbonate. This resulted in the precipitation of a white solid that was filtered, washed with water, and air-dried. Recrystallization of the crude product from a saturated solution of methanol-water (2:1 v/v) afforded the title compound. Yield: 3.3 g (75%). Anal. Calcd for $C_{21}H_{19}N_3O_4{:}$ C, 66.83; H, 5.07; N, 11.13. found: C, 66.70; H, 4.97; N, 11.16. FT-IR (KBr, cm⁻¹): ν 3280 (NH), 1652, 1667 (C=O). ¹H NMR (300 MHz, DMSO- d_6): δ 3.76 (s, 6H, OCH₃), 6.99 (d, J = 7.5 Hz, 4H, H₁₀ and H_{12}), 7.77 (d, J = 9.1 Hz, 4H, H_9 and H_{13}), 8.28 (t, J = 7.8 Hz, 2H, H_4), 8.35 (d, J = 7.3 Hz, 1H, H_3 and H_5), 10.92 (s, 2H, NH-C=O). ¹³C NMR (300 MHz, DMSO- d_6): δ 140.13 (C₄), 125 (C₃ and C₅),

148.83 (C₂ and C₆), 160.74 (C₇), 131.06 (C₈), 122.90 (C₉ and C₁₃), 113.89 (C₁₀ and C₁₂), 156.01 (C₁₁), 55.22 (OCH₃). MS (EI⁺, m/z): calcd 377.14, found 378.02 [M + H]⁺.

2,6-Bis(3-methoxy-benzene-carbamoyl)pyridine (H_2L^{m-OMe}) . This ligand was synthesized in a similar manner as discussed for H_2L^{p-OMe} with following reagents: pyridine-2,6-dicarboxylic acid (2.0 g, 0.011 mol), 3-methoxy aniline (2.94 g, 0.023 mol), and triphenylphosphite (7.4 g, 0.023 mol). Yield: 3.25 g (72%). Anal. Calcd for $C_{21}H_{19}N_3O_4$: C, 66.83; H, 5.07; N, 11.13. found: C, 67.06; H, 4.88; N, 11.67. FT-IR (KBr, cm⁻¹): ν 3294 (NH), 1665, 1679 (C=O). ¹H NMR (300 MHz, DMSO- d_6): δ 3.79 (s, 6H, -OCH₃), 6.77 (d, J = 8.24 Hz, 2H, H_{11}), 7.35 (t, J = 8.34 Hz, 2H, H_{13}), 7.47 (d, J = 7.9 Hz, 2H, H_{12}), 7.62 (s, 2H, H₉), 8.31 (t, J = 7.34 Hz, 1H, H₄), 8.39 (d, J = 7.32 Hz, 1H, H₅ and H₃), 10.99 (s, 2H, NH-C=O). ¹³C NMR (300 MHz, DMSO- d_6): δ 139.23 (C₄), 125.42 (C₃ C₅), 148.83 (C₂ C₆), 161.69 (C₇), 140.03 (C₈), 106.83 (C₉), 159.54 (C₁₀), 109.76 (C₁₃), 129.63 (C₁₂), 113.32 (C₁₁), 55.11 (OCH₃). MS (EI⁺, m/z): calcd 377.14, found 377.82 [M + H]⁺.

2,6-Bis(3,4-methylinedioxy-benzene-carbamoyl)-pyridine (H_2L^{md}) . This ligand was also synthesized in a similar manner as mentioned for H_2L^{p-OMe} with following reagents: pyridine-2,6-dicarboxylic acid (2.0 g, 0.011 mol), 3,4-methylenedioxy aniline (3.28 g, 0.023 mol), triphenylphosphite (7.4 g, 0.023 mol). Yield: 3.8 g (78%). Anal. Calcd for $C_{21}H_{15}N_3O_6$: C, 62.22; H, 3.73; N, 10.73. found: C, 61.93; H, 4.17; N, 10.36. FT-IR (KBr, cm⁻¹): ν 3274 (N–H), 1666, 1650 (C=O). ¹H NMR (300 MHz, DMSO- d_6): δ 6.00 (s, 4H, OCH₂), 6.84 (d, *J* = 6.3 Hz, 2H, H₁₂), 7.30 (d, *J* = 6.3 Hz, 2H, H₁₃), 7.56 (s, 2H, H₉), 8.14 (t, *J* = 5.8 Hz, 1H, H₄), 8.42 (d, *J* = 5.8 Hz, 2H, H₃ and H₅). ¹³C NMR (300 MHz, DMSO- d_6): δ 101.23 (OCH₂), 103.18 (C₉), 108.07 (C₁₂), 114.48 (C₁₃), 125.14 (C₃ and C₅), 132.23 (C₈), 139.93 (C₄), 143.88 (C₁₁), 147.15 (C₁₀), 148.78 (C₂ and C₆), 161.34 (C₇). MS (EI⁺, *m*/z): calcd 405.10, found 406.10 [M + H]⁺.

Synthesis of Co³⁺ Complexes with Protected Phenol and Catechol Groups. $Na[Co(L^{p-OMe})_2].2CH_3OH$ (1^p). The ligand $H_{3}L^{\text{p-OMe}}$ (0.100 g, 0.264 mmol) was dissolved in DMF (10 mL) and deprotonated with the solid NaH (0.013 g, 0.529 mmol) under magnetic stirring. The mixture was stirred for 15 min. Solid $[Co(H_2O)_6](ClO_4)_2$ (0.048 g, 0.132 mmol) was added to the above said mixture under magnetic stirring. After 30 min of stirring, dry O₂ was purged to the solution for 2 min. The solution was finally stirred for additional 1 h. The reaction mixture was filtered followed by the removal of solvent under reduced pressure. The crude product was isolated after washing with diethyl ether. The crude product thus obtained was redissolved in DMF and subjected to vapor diffusion of diethyl ether. This resulted in a highly crystalline product within a day. Yield: 0.154 g (70%). Anal. Calcd. for C42H34CoN6NaO8·2CH3OH: C, 58.93; H, 4.72; N, 9.37. found: C, 59.19; H, 4.70; N, 9.80. ¹H NMR (300 MHz, DMSO- d_6): δ 3.56 (s, 12H, OCH₃), 6.44 (d, J = 8.7 Hz, 8H, H₁₀ and H₁₂), 6.57 (d, J = 9.0 Hz, 8H, H₉ and H₁₃), 7.50 (d, J =7.8 Hz, 4H, H₃ and H₅), 7.90 (t, J = 7.8 Hz, 1H and H₄). ¹³C NMR (300 MHz, DMSO- d_6): δ 138.74 (C₈), 122.59 (C₃ and C₅), 155.29 (C₆), 166.73 (C₇), 138.64 (C₄), 126.60 (C₉ and C₁₃), 112.99 (C₁₀ and C₁₂), 156.33 (C₁₁), 54.99 (OCH₃). FT-IR (KBr, cm⁻¹): ν 3073, 2934, 2834 (C–H), 1676, 1585 (C=O). Absorption spectrum (DMF, λ_{max}) nm (ε , M⁻¹ cm⁻¹): 627 (15), 464 (sh, 200), 299 (sh, 1412). Conductivity (DMF, ~1 mM solution, 298 K): $\Lambda_{\rm M} = 60 \ \Omega^{-1} \ {\rm cm}^2$ mol⁻¹. MS (EI⁺, m/z): calcd 832.17, found 833.09 [M + H]⁺.

Na[*Co*(*L*^{*m*-OMe})₂] (2^{*P*}). This complex was synthesized in a similar manner with an identical scale as discussed for complex 1^P. Yield: 0.158 g (72%). Anal. Calcd for C₄₂H₃₄CoN₆NaO₈·CH₃OH·3H₂O: C, 56.21; H, 4.83; N, 9.15. found: C, 56.58; H, 4.39; N, 9.39. ¹H NMR (300 MHz, DMSO-*d*₆): δ 3.48 (s, 6H, OCH₃), 6.21 (s, 2H, H₉), 6.26 (d, *J* = 8.0 Hz, 2H, H₁₁), 6.37 (d, *J* = 7.7 Hz, 2H, H₁₃), 6.47 (t, *J* = 8.0 Hz, 2H, H₁₂), 7.48 (d, *J* = 8.0 Hz, 2H, H₃ & H₅), 7.86 (t, *J* = 7.8 Hz, 1H, H₄). ¹³C NMR (300 MHz, DMSO-*d*₆): δ 109.92 (C₉), 110.82 (C₁₃), 118.65 (C₁₁), 122.80 (C₃ and C₅), 128.30 (C₁₂), 138.98 (C₈), 147.20 (C₄), 156.39 (C₂ and C₆), 158.78 (C₁₀), 166.49 (C₇), 54.55 (OCH₃). FT-IR (KBr, cm⁻¹): *ν* 2930 (C–H) 1663, 1605 (C==O). Absorption spectrum (DMF, λ_{max} nm (ε, M⁻¹ cm⁻¹): 635 (10), 470 (sh, 102), 299 (6220). Conductivity (DMF, ~1 mM solution at

298 K): $\Lambda_{\rm M}$ = 65 Ω^{-1} cm² mol⁻¹. MS (EI⁺, *m*/*z*): calcd 832.17, found 833.04 [M + H]⁺.

 $(H_3O^+)[Co(L^{md})_2]$ (3^P). This complex was again synthesized in a similar manner as discussed for complex 1^P with following reagents: H₂L^{md}: 0.100 g (0.246 mmol); NaH: 0.011 g (0.493 mmol), [Co(H₂O)₆](ClO₄)₂ 0.045 g (0.123 mmol). Yield: 0.155 g (75%). Anal. Calcd for H₃O⁺·C₄₂H₂₆CoN₆O₁₂·2H₂O: C, 54.79; H, 3.61; N, 9.13. found: C, 54.94; H, 3.19; N, 9.47. ¹H NMR (300 MHz, DMSO-d₆): δ 5.85 (s, 4H, -CH₂-), 6.09 (d, J = 8.0 Hz, 2H, H₁₂), 6.17 (s, 2H, H₉), 6.47 (d, J = 8.1 Hz, 2H, H₁₃), 7.65 (d, J = 7.7 Hz, 2H, H₃ and H₃), 8.03 (t, J = 7.6 Hz, 1H, H₄). ¹³C NMR (300 MHz, DMSO-d₆): δ 100.58 (OCH₂), 100.93 (C₉), 107.31 (C₁₂), 118.37 (C₁₃), 122.98 (C₅ and C₃), 139.18 (C₈), 139.89 (C₄), 143.14 (C₁₁), 146.43 (C₁₀), 156.20 (C₂ and C₆). 166.83 (C₇). FT-IR (KBr, cm⁻¹): ν 2923, 2855 (C-H), 1588, 1502 (C=O). Absorption spectrum (DMF, λ_{max} nm (ε , M⁻¹ cm⁻¹): 636 (12), 463 (sh, 450), 317 (sh, 2640). Conductivity (DMF, ~1 mM solution at 298 K): $\Lambda_{\rm M}$ = 60 Ω^{-1} cm⁻¹. MS (EI⁺, *m*/*z*): calcd 888.08, found 888.90 [M + Na]⁺.

Synthesis of Co³⁺ Complexes with Deprotected Phenol and Catechol Groups. $(H_3O^+)[Co(L^{p-OH})_2]$ (1). The compound Na[Co- $(L^{p-OMe})_2$] (1^P) (0.5 g, 0.6 mmol) was dissolved in 40 mL of dry and degassed CH₂Cl₂ under magnetic stirring. BBr₃ (0.28 mL, 3.0 mmol) was carefully introduced to the aforementioned solution under the dinitrogen atmosphere. The resulting red-brown slurry was stirred for 4 h at -70 °C. The excess BBr₃ was slowly quenched with the addition of MeOH. Evaporation of the solvent under vacuum afforded a brown solid which was further recrystallized from the methanol. Yield: 0.26 g (55%). Anal. Calcd. for $H_{3}O^{+}\!\cdot\!C_{38}H_{26}CoN_{6}O_{8}{\cdot}6H_{2}O{\cdot}$ C, 51.82; H, 4.69; N, 9.54. Found: C, 51.53; H, 4.59; N, 9.67. ¹H NMR (300 MHz, DMSO- d_6): δ 6.20 (d, J = 8.0 Hz, 4H, H₁₀ and H₁₂), 6.39 (d, J = 9.5 Hz, 4H, H₉ and H₁₃), 7.45 (d, J = 8.0 Hz, 2H, H₃ and H₅), 7.87 (t, J = 7.7 Hz, 1H, H₄). ¹³C NMR (300 MHz, DMSO- d_6): δ 114.21 (C₁₀ and C₁₂), 122.24 (C₃ and C₅), 126.44 (C₉ and C₁₃), 137.27 (C₄), 138.36 (C_8) , 153.04 (C_6) , 156.46 (C_{11}) , 166.67 (C_7) . FT-IR (KBr, cm⁻¹): ν 3400 (O-H), 1664, 1570 (C=O). Absorption spectrum (DMF, λ_{max} nm (ϵ , M⁻¹ cm⁻¹): 642 (45), 473 (sh, 1830), 315 (sh, 920). Conductivity (DMF, ~1 mM solution at 298 K): $\Lambda_{\rm M} = 55 \ \Omega^{-1} \ {\rm cm}^2$ $mo\Gamma^{-1}$. MS (EI⁺, m/z): calcd 776.10, found 777.07 [M + Na]⁺.

 $(H_3O^+)[Co(L^{\dot{m}-OH})_J]$ (2). This complex was synthesized in a similar manner with an identical scale as discussed for compound 1. Yield: 0.24 g (52%). Anal. Calcd for $H_3O^+C_{38}H_{26}CoN_6O_86H_2O$: C, 51.90; H, 5.01; N, 9.08. found: C, 52.05; H, 5.12; N, 8.73. ¹H NMR (300 MHz, DMSO- d_6): δ 6.08 (d, J = 7.56 Hz, 2H, H_{11}), 6.14 (s, 2 H, H_9), 6.23 (d, J = 8.0 Hz, 2 H, H_{13}), 6.59 (t, J = 7.9 Hz, 2 H, H_{12}), 7.49 (d, J = 7.7 Hz, 2 H, H_3 and H_5), 7.88 (t, J = 7.3 Hz, 1 H, H_4). ¹³C NMR (300 MHz, DMSO- d_6): δ 111.44 (C₉), 113.29 (C₁₃), 117.25 (C₁₁), 123.47 (C₃ and C₅), 128.84 (C₁₂), 139.53 (C₈), 146.61 (C₄), 156.46 (C₂ and C₆), 157.03 (C₁₀), 166.95 (C₇). FT-IR (KBr, cm⁻¹): ν 3417 (OH), 1602 (C=O). Absorption spectrum (DMF, λ_{max} nm (ε , M^{-1} cm⁻¹): 642 (15), 469 (sh, 270), 304 (sh, 220). Conductivity (DMF, ~1 mM solution at 298 K): $\Lambda_M = 60 \ \Omega^{-1} \ cm^{-1}$. MS (EI⁺, m/z): calcd 776.10, found 777.05 [M + Na]⁺.

(*H*₃O⁺)[Co(*L*^{cat})₂] (**3**). The complex **3** was also synthesized using an identical procedure with similar scale as discussed for compound **1**. Yield: 0.28 g (60%). Anal. Calcd for H₃O⁺C₃₈H₂₆CoN₆O₈·4H₂O: C, 50.23; H, 4.10; N, 9.25. Found: C, 50.43; H, 4.31; N, 9.34. ¹H NMR (300 MHz, DMSO-*d*₆): δ 5.98 (d, *J* = 7.9 Hz, 2H, H₁₂), 6.23 (d, *J* = 7.9 Hz, 2H, H₁₃), 6.27 (s, 2H, H₉), 7.66 (d, *J* = 7.6 Hz, 2H, H₃ and H₅), 7.98 (t, *J* = 7.8 Hz, 1H, H₄). ¹³C NMR (300 MHz, DMSO-*d*₆): δ 113.51 (C₉), 114.72 (C₁₂), 116.55 (C₁₃), 123.17 (C₅ and C₃), 137.02 (C₈), 141.89 (C₄), 144.52 (C₁₁ and C₁₀), 156.35 (C₂ and C₆), 166.89 (C₇). FT-IR (KBr, cm⁻¹): ν 3420 (O–H), 1563, 1517 (C=O). Absorption spectrum (DMF, λ_{max} , nm (ε , M⁻¹ cm⁻¹): 638 (15), 456 (sh, 105), 330 (sh, 400). Conductivity (DMF, ~1 mM solution at 298 K): $\Lambda_{\rm M}$ = 58 Ω^{-1} cm² mol⁻¹. MS (EI⁺, *m*/*z*): calcd 840.08, found 841.09 [M + Na]⁺.

Physical Methods. The FT-IR spectra (KBr disk, $4000-400 \text{ cm}^{-1}$, 0.12 cm⁻¹ resolution) were recorded on a Perkin-Elmer FTIR 2000 spectrometer. Absorption spectra were obtained from the Perkin-Elmer *Lambda*-25 spectrophotometer. ESI-MS mass spectra were

measured with the LC-TOF (KC-455) mass spectrometer of Waters. ¹H NMR and ¹³C NMR spectra were recorded either on Avance Bruker (300 MHz) or Jeol (400 MHz) instrument with TMS as the internal standard. Microanalytical data were obtained from the Elementar Analysen Systeme GmbH Vario EL-III instrument. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies were performed on DTG - 60 SHIMADZU and TA DSC Q 200 instruments, respectively, at 5 °C/min heating rate under the dinitrogen atmosphere. X-ray powder diffraction (XRPD) patterns were recorded using a Bruker AXS D8 Discover (Cu-K α radiation, $\lambda = 1.54184$ Å) diffractometer. The samples were ground and subjected to the range of 2θ -50 θ with a step size of 0.02° in 2θ angle. The nitrogen sorption isotherms were measured with an ASAP 2020 V3.00H Micromeritices, USA instrument in a standard volumetric technique at 177 K. Under continuous adsorption conditions, prior to measurements, samples were heated at 150 °C for 12 h with helium gas used for flushing purposes.

Crystallography. Single crystals suitable for the X-ray diffraction for complexes 1^{P} , 3^{P} , 1, 2, and 3 were grown by the slow diffusion of diethyl ether or isopropyl ether to a methanol solution of compound at room temperature. X-ray diffraction data were collected on a Bruker AXS SMART Apex CCD diffractometer using MoK α radiation ($\lambda = 0.71073$ Å).^{20a,b} The intensity data were corrected for the Lorentz and polarization effects.^{20c} The multiscan absorption correction was also applied.^{20c} The structures were solved by the direct methods using SIR-97²¹ and refined by full-matrix least-squares method on F^2 (SHELXL-97).²² All calculations were carried out using the WinGX crystallographic package.²³ The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with U_{iso} values of 1.2, 1.2, and 1.5 times the U_{iso} values of methylene, phenylene, and methyl carbon atoms, respectively. Notably, the data for complexes 2 and 3 were measured in nonstandard space group I222. The refinement of complex 1 showed an oxygen atom with the site occupancy factor (SOF) of 0.25, which was modeled as the hydronium ion (H_3O^+) ; however, the hydrogen atoms of this ion could not be located because of the partial occupancy. These hydrogen atoms were included in the molecular formula, however. Apart from this hydronium ion, there was still some unaccountable electron density which is most likely due to a few disordered solvent molecules, but it was too diffused to be modeled accurately. Therefore, it was removed by using the SQUEEZE routine of the PLATON program.²⁴ Such a treatment improved the model tremendously and the R factor decreased from ca. 0.09 to ca. 0.05. The structure also showed solvent accessible voids (SAV) of volume 1282 Å3. The latter were present even before squeezing out the disordered solvent molecules, however, with a much smaller volume of 181 Å³. Both complexes 2 and 3 also showed disordered water molecules apart from the complex anion. These oxygen atoms were refined with the SOF of 0.25 which significantly improved their thermal parameters in comparison to their refinement with full site occupancy of 1. Such oxygen atoms were modeled as the hydronium ions whose hydrogen atoms could not be located. Their molecular formulas include these hydrogen atoms. The crystal structures of both complexes 2 and 3 contain SAVs of volumes 277 and 317 Å³, respectively, due to the crystal packing. The refinement of complex 3^P showed an oxygen atom with an SOF of 0.5. As this O atom was on special position and two hydrogen atoms could be located easily, one of them was refined with an SOF of 1 while the other one with an SOF of 0.5. This generates an H₃O⁺ ion with one of its hydrogen atoms being disordered over two positions with 50% site occupancy. For this complex, the model again shows SAVs of volume 274 Å³ due to packing interactions. The crystallographic data collection and structure refinement parameters for all complexes are summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis and Characterization. The complexes 1–3 were synthesized starting with the ligands containing protected phenol $(H_2L^{p-OMe} \text{ or } H_2L^{m-OMe})$ or catechol (H_2L^{md}) groups, preparing their Co³⁺ complexes (1^P-3^P) , and subsequent

deprotection using BBr_3 (Scheme 3). The complexes 1-3 were isolated as the deep red-brown crystalline solids, and their DMF solutions display absorption maxima at ca. 650 nm (Figures S1-S3, Supporting Information). Complexes 1-3 are monoanionic in nature and the charge is balanced by the protonated form of the water molecule (i.e., hydronium ion, H_3O^+). The evidence for the presence of H_3O^+ has come from the conductivity data (that shows a 1:1 electrolytic nature) and pH measurements (the pK_a was observed below 4 for all three complexes).²⁵ The protonation that resulted in the generation of H_3O^+ ion has most probably occurred during the deprotection step involving BBr₃ (the reaction generates HBr). The deprotected complexes 1-3 show broad signals at 3402, 3368, and 3234 cm⁻¹, respectively, which we assign to $\nu_{\rm O-H}$ of the phenolic group²⁶ (Figure S4, Supporting Information). Notably such stretches were absent in their precursor protected molecules $1^{P}-3^{P}$. In addition, the proton NMR spectra displayed a broad feature between 3-4 ppm for the presence of a phenolic -OH group which disappeared on the addition of D₂O (Figures S5-S10, Supporting Information). All complexes were also characterized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The TGA profiles of complexes 1 and 2, respectively, show ca. 15.2% and 13.7% weight loss between 25-115 °C that fits nicely with the calculated weight loss of ca. 14.4% for the elimination of six water molecules and one hydronium ion²⁷ (Figure S11, Supporting Information). Notably, the microanalytical data for both complexes 1 and 2 support the presence of six water molecules and one hydronium ion. Furthermore, the crystallographic studies also suggest the presence of unaccountable electron density which is most likely due to the disordered water molecules. Similarly, for complex 3, the initial weight loss (obs. 9.2%) describes the release of four water molecules and one hydronium ion²⁷ that match well with the calculated value of 10.02%. The presence of four water molecules and one hydronium ion in complex 3 is again supported by the microanalytical results. Complex 1^P shows the weight loss (obs. 6.7%) due to the release of two methanol molecules that nicely matches with the calculated value of 7.14%. For complex 2^P, the observed weight loss of 9.6% describes the release of one methanol and three water molecules that fits well with the calculated value of 9.3%. The observation of voids in the crystal structure of complex 3^{P} is strongly justified by the thermal weight loss due to one hydronium ion²⁷ and four water molecules, although the microanalytical data suggest the presence of only two water molecules in addition to a hydronium ion.

The thermal studies were followed by X-ray powder diffraction (XRPD) studies to understand the effect of solvent removal (guest water molecules) on the H-bonded network's stability. For all three deprotected complexes, it was observed that the H-bonded networks are stable up to 75 °C; however, when the temperature was raised to 150 °C, crystallinity was partially lost as evidenced by broad features in the XRPD patterns (Figures S12-S14, Supporting Information). The deprotected complexes 1, 2, and 3 were also analyzed for their gas sorption properties owing to their crystallographically observed void structures (cf. crystal structures). The N2 sorption studies indicated poorly porous structures with BET surface area of 1.23, 2.53, and 3.67 m^2/g for complexes 1, 2, and 3, respectively (Figures S15-S17, Supporting Information). The observed low porosity suggest that most of the available space is being occupied by the building blocks themselves, thus

Table 1. Data Collection and Structure Solution Parameters for Complexes $Na[Co(L^{p-OMe})_2]$ ·2CH₃OH (1^p), H₃O⁺[Co(L^{m-OH})_2] (1), H₃O⁺[Co(L^{m-OH})_2] (2), and H₃O⁺[Co(L^{cat})_2] (3)

	1^{p}	3 ^p	1	2	3
formula	C44H42CoN6NaO10	C42H29CoN6O13	C38H29CoN6O9	C38H29CoN6O9	C38H29CoN6O13
fw	896.76	784.64	772.60	772.60	836.60
T (K)	298(2)	298(2)	293(2)	293(2)	293(2)
crystal system	monoclinic	trigonal	tetragonal	orthorhombic	orthorhombic
space group	$P2_1/c$	R3c	I I	I222	I222
a (Å)	13.9491(7)	25.186(2)	13.948(5)	10.039(4)	10.3708(3)
b (Å)	18.6397(7)	25.186(2)	13.948(5)	15.446(5)	15.3526(5)
c (Å)	16.798(1)	33.184(3)	13.771(5)	14.872(5)	15.0072(6)
α (°)	90	90	90	90	90
β (°)	101.633(7)	90	90	90	90
γ (°)	90	120	90	90	90
V (Å ³)	4277.9(4)	18230(2)	2679(2)	2306.1(14)	2389.43(14)
Ζ	4	18	2	2	2
$d (g \text{ cm}^{-3})$	1.392	1.450	0.958	1.113	1.163
F(000)	1864	8172	796	796	860
goodness of fit (F^2)	0.990	1.273	1.002	1.110	1.026
$R_1, wR_2 [I > 2 (I)]$	$R_1 = 0.0681$	$R_1 = 0.0806$	$R_1 = 0.0515$	$R_1 = 0.1120$	$R_1 = 0.0783$
	$wR_2 = 0.1811$	$wR_2 = 0.2024$	$wR_2 = 0.1281$	$wR_2 = 0.2871$	$wR_2 = 0.2198$
R_1 , w R_2 [all data]	$R_1 = 0.1025$	$R_1 = 0.0845$	$R_1 = 0.0684$	$R_1 = 0.1239$	$R_1 = 0.0978$
	$wR_2 = 0.1976$	$wR_2 = 0.2052$	$wR_2 = 0.1350$	$wR_2 = 0.3059$	$wR_2 = 0.2277$

Scheme 3. Preparative Routes for the Protected Complexes $1^{P}-3^{P}$ and Their Deprotected Complexes $1-3^{a}$



^aConditions: (a) 2 equiv of NaH, DMF, N₂; (b) 0.5 equiv of $[Co(H_2O)_6](ClO_4)_{2}$; (c) excess O₂; (d) 5 equiv of BBr₃, CH₂Cl₂, -70 °C.

significantly reducing the sorption properties. Our earlier $\{Co^{3+}-Zn^{2+}\}$ and $\{Co^{3+}-Cd^{2+}\}$ networks have also shown a similar moderate porous behavior due to the space occupying nature of the building blocks. 17e,f

Crystal Structures. Protected complexes 1^{P} and 3^{P} and the deprotected complexes 1, 2, and 3 were crystallographically

characterized. Table 1 contains the data collection and structure refinement parameters, whereas Tables 2–4 display the bonding and hydrogen bonding parameters, respectively. Subsequent sections discuss the molecular structures and their organization through various H-bonding and other noncovalent interactions.

Article

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes 1^{p} and 3^{pa}

$Na[Co(L^{p-OMe})_2$]·2CH ₃ OH (1^{P})	$H_{3}O^{+}[Co(L^{MD})_{2}](3^{P})$					
Around Co ³⁺ Ion							
Co1-N1	1.842(2)	Co1-N1	1.855(3)				
Co1-N2	1.956(3)	Co1-N2	1.972(3)				
Co1-N3	1.959(3)	Co1-N3	1.955(3)				
Co1-N4	1.853(2)	N1-Co1-N1 ⁱ	174.1(2)				
Co1-N5	1.964(2)	N1-Co1-N3	81.00(14)				
Co1-N6	1.968(2)	N1-Co1-N3 ⁱ	94.93(13)				
N1-Co1-N4	177.62(11)	N3-Co1-N3 ⁱ	93.10(12)				
N1-Co1-N2	82.07(10)	N1-Co1-N2 ⁱ	102.20(15)				
N4-Co1-N2	95.60(11)	N1 ⁱ -Co1-N2 ⁱ	81.94(14)				
N4-Co1-N5	81.61(10)	N2 ⁱ -Co1-N3 ⁱ	162.87(14)				
N4-Co1-N3	100.70(11)	N2-Co1-N3 ⁱ	89.81(14)				
N1-Co1-N5	97.93(10)	N2-Co1-N2 ⁱ	92.32(19)				
N1-Co1-N6	98.64(10)						
N4-Co1-N6	81.83(10)						
N3-Co1-N6	92.65(10)						
N5-Co1-N6	163.43(10)						
Around Na ⁺ Ion							
Na-O1	2.231(3)						
Na-O2	2.311(2)						
Na-O3	2.271(3)						
Na-O10	2.285(3)						
a(:) C		.]					

"(i) Symmetry transformations used to generate equivalent atoms for complex 3^{P} : x - y + 1/3, -y + 2/3, -z + 13/6.

Complex 1^P. The crystal structure of complex 1^{P} is shown in Figure 1, whereas Table 2 displays the selected bond distances and bond angles. Complex 1^{P} crystallized in the monoclinic cell system and the space group $P2_{1}/c$. The asymmetric unit contains one complex anion, one Na⁺ cation, and two methanol molecules. The molecular structure of complex anion shows that the Co³⁺ ion is coordinated by two protected tridentate ligands in their dianionic form, $[L^{p-OMe}]^{2-}$. The cobalt ion is bound to four N_{amide} atoms (avg. Co-N_{amide}: 1.962(2) Å) in the basal plane and two $N_{pyridine}$ atoms (avg. $Co-N_{pyridine}$: 1.848(2) Å) in the axial position (Figure 1a). This results in an octahedral geometry around the Co(III) ion. Complex 1^P shows interesting solid-state packing where three O_{amide} groups are coordinated to three symmetry related Na⁺ ions (avg. Na····O_{amide}: 2.271(3) Å), while the fourth O_{amide} group forms a H-bond with the methanol molecule $(O_{methanol} \cdots O_{amide}: 2.699(6)\text{Å})$ (Figure 1b). Notably, each Na⁺ ion acts as the nodal point and connects three different anionic molecules together (Figure 1c). The fourth coordination of the sodium ion comes from the oxygen atom of the second methanol molecule (Na···O_{MeOH}: 2.285(3) Å). Thus, the geometry around the Na⁺ ion is tetrahedral (Figure 1c). The overall bonding between Na⁺ ions and complex anions result in the formation of a zigzag chain propagating along the c-axis. Two such chains are further connected to each other via an Hbond between two methanol molecules (O10---O9ⁱⁱ: 2.709(6) Å) (Figure 1d,e, Table 4). Thus, an array of H-bonds involving O_{amide} (O4), O_{methanol} (O9), O_{methanol} (O10), and Na⁺ connect two chains together (Table 4). In addition, several weak $C-H\cdots O$ H-bonding interactions exist involving O_{amide} (O2) and O3) and O_{methoxy} (O7) and hydrogen atoms connected to pyridyl, methoxy, and anisidyl groups (see Table S1, Supporting Information).

Complex 3^P. Complex 3^P crystallized in the trigonal cell system with $R\overline{3}c$ space group. The charge on the anionic metal complex is balanced by a hydronium ion (i.e., H_3O^+). The molecular structure of complex anion shows that the Co³⁺ ion is coordinated by four N_{amide} atoms (avg. Co-N_{amide}: 1.963(3) Å) in the basal plane and two N_{pyridine} atoms (avg. Co-N_{pyridine}:

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes $1-3^a$

	$H_{3}O^{+}[Co(L^{p-OH})_{2}]$ (1)	$H_{3}O^{+}[Co(L^{m-OH})_{2}]$ (2)	$H_{3}O^{+}[Co(L^{cat})_{2}]$ (3)
Co1-N1	1.846(4)	1.828(9)	1.853(4)
Co1-N2	1.952(2)	1.939(7)	1.966(4)
$N1-Co1-N1^{i(1),ii(2),iii(3)}$	180	180	180
N1-Co1-N2	81.96(6)	81.26(17)	81.64(9)
$N1-Co1-N2^{i(1),ii(2),iv(3)}$	98.04(6)	98.74(17)	98.36(9)
$v^{(1)}N2-Co1-N2^{i(1),ii(2),iii(3)}$	91.12(16)	90.0(4)	94.4(2)
^{v(1)} N2-Co1-N2 ^{vi(2),vii(3)}	163.92(11)	162.50(3)	163.27(18)
$N2-Co1-N2^{viii(1),vii(2),iv(3)}$	91.12(16)	92.7(4)	88.1(2)

^aSymmetry transformations used to generate equivalent atoms: (i) -x + 1/2, y + 1/2, -z + 3/2; (ii) x, -y + 2, -z; (iii) -x, -y, z; (iv) x, -y, -z; (v) -x + 1, -y, z; (vi) -x, -y + 2, z; (vii) -x, -y, -z; (viii) x - 1/2, -y + 1/2, -z + 3/2.

Tab	le 4.	Some	Important	H-Bond	Parameters	for	Comp	lexes	1 ^P	, 3ª	', and	1-	-3"
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complex	D-H…A	$d(H \cdots A)$ (Å)	$d(D \cdots A)$ (Å)	\angle (DHA) (°)
$Na[Co(L^{p-OMe})_3] \cdot 2CH_3OH(1^p)$	O9-H9 O4 ⁱ	2.06	2.699(6)	135
	O10-H10····O9 ⁱⁱ	1.74	2.709(6)	174
$H_{3}O^{+}[Co(L^{MD})_{3}]$ (3 ^P)	07–H71…01 ⁱⁱⁱ	1.73	2.769(4)	167
	O7-H72···O2 ^{iv}	1.67	2.789(7)	169
$H_3O^+[Co(L^{p-OH})_3]$ (1)	O2-H2A···O1 ^v	1.88	2.689(4)	171
$H_3O^+[Co(L^{m-OH})_3]$ (2)	O2-H2A···O1 ^{vi}	1.81	2.610(11)	164
$H_3O^+[Co(L^{cat})_3]$ (3)	O2-H21-···O3 ⁱ	2.23	2.688(5)	114
	O2-H21…O1 ^{vii}	1.84	2.585(5)	148
	O3-H31O2 ^{viii}	1.85	2.664(5)	163

^aSymmetry transformations used to generate equivalent atoms: (i) *x*, *y*, *z*; (ii) -x, +y + 1/2, -z + 1/2 + 1; (iii) *y*, +x, -z + 1/2 + 1; (iv) y - 1/3, -x + y + 1/3, -z + 1/3 + 1; (v) -x + 1/2, -y + 1/2, +z + 1/2; (vi) -x + 1/2, +y - 1/2, -z - 1/2; (viii) x + 1/2, -y - 1/2, -z - 1/2.

Crystal Growth & Design



Figure 1. (a) Molecular structure of the anionic part of complex $\mathbf{1}^{P}$ (thermal ellipsoids are drawn at the 40% probability level; only methoxy hydrogen atoms are shown for clarity); (b) shows the arrangement of different components in the unit cell; (c) shows the coordination environment of Na⁺ ion; (d) shows interaction between different components that results in the generation of a 2D network (view along the *b* axis); (e) shows a small portion of panel (d) depicting hydrogen bonding involving O_{amide} (O4) and two methanol molecules (with atoms O9 and O10). See text for detail.

1.855(3) Å) in the axial position (Figure 2a) resulting in an octahedral geometry around the metal. The hydronium ion, present to balance the charge of anionic complex, takes part in unique H-bonding with the complex anions. Notably, due to the site occupancy factor and the special position of oxygen atom, the hydronium ion was modeled with one of the hydrogen atoms disordered over two positions with 50% probability; as a result it (O7) was making H-bonds with four different complex anions (Figure 2b). These H-bonds were formed between O_{amide} atoms (O1 and O2 and their symmetry related atoms) and the hydrogen atoms attached to the $O_{hydronium}$ ion. The heteroatom separations $O7{\cdots}O1^{iii}$ and $O7 \cdots O2^{iv}$ were observed to be 2.769(4) and 2.789(7) Å, respectively (Table 4). A c-axis view shows that 18 complex anions in conjunction with equal number of hydronium ions were creating a hexagonal unit (Figure 2c). These hexagonal units were further connected to each other to generate a honey-comb like network (Figure 2d). The said network further get strengthened by the presence of C-H…O H-bonding interactions between the oxygen atom of methylenedioxy group (O3) and the hydrogen atom attached to the pyridine ring (C10) (see Table S1, Supporting Information).

Crystal Structures and Self-Assembly of Complexes 1-3. The molecular structures for all three deprotected complexes (1-3) are quite similar and show that the central Co^{3+} ion is meridionally coordinated by two tridentate ligands. The octahedral cobalt(III) ion is bonded by four N_{amide} atoms in the basal plane and two $N_{\mbox{\scriptsize pyridine}}$ atoms in the axial position (Figures 3a-5a). The $Co-N_{amide}$ and $Co-N_{pvridine}$ distances were found to be in the range of 1.939(7) - 1.966(4) Å and 1.828(9)-1.853(4) Å, respectively (Table 3). Two axial pyridine rings were trans to each other, whereas the diagonal N_{amide} groups make angle with the central Co(III) ion nearly 163° in all three cases (Table 3). Notably, these molecules are equipped with the peripheral H-bonding donor -OH groups and have the ability to self-assemble considering the fact that there are H-bonding acceptors in O_{amide} groups. Thus, all three molecules self-assemble into complementary supramolecular



Figure 2. (a) Molecular structure of the anionic part of complex 3^{P} (thermal ellipsoids are drawn at 40% probability level); (b) molecular architecture formed by O–H…O interactions between the hydrogen atoms of hydronium ion and O_{amide} atoms from complex anions; (c) arrangement of complex anions and hydronium ions that result in the generation of a hexagonal structure (view along the *c*-axis); and (d) additional H-bonding interactions between hexagonal units generates a honeycomb structure (view along the *c*-axis). See text for detail.

networks via intermolecular H-bonding between OH and $C=O_{amide}$ groups.

Complex 1 crystallized in a highly symmetrical tetragonal cell system with $I\overline{4}$ space group (Figure 3). In this molecule, the intermolecular H-bonding takes place between *p*-phenolic OH and C=O_{amide} groups in a highly symmetrical fashion. Interestingly, due to the octahedral geometry of the metal, the H-bonding donor (OH) and H-bonding acceptor (O_{amide}) groups are placed above and below in an alternate manner. Thus, the central molecule is able to interact simultaneously with eight neighboring molecules via OH…C=O_{amide} H-bonds (Figure 3b,c, shown by two shades of green color). The phenolic O-H group (O2-H2A) interacts with the complementary C=O_{amide} oxygen atom O1, forming the O2-H2A…O1^v motif (Figure 3b,c; Table 4)

with the heteroatom separation between any such pair being 2.689(4) Å, while the O–H···O_{amide} angle was found to be 171°. In this compound, the negative charge on the complex anion was balanced by the presence of a hydronium ion (H₃O⁺). Notably, the hydronium ion which is present within the H–bonded network was found without significant interactions. We believe that the highly symmetrical array of H-bonds between phenolic OH and O_{amide} groups has prevented these functional groups from further interacting with the hydronium ion. In fact, a somewhat different situation was noticed in complex 2 with the *m*-phenol appended group where the hydronium ion showed significant interactions with O_{amide} groups (cf. crystal structure of complex 2). The space filling diagram of complex 1 shows solvent accessible voids (SAVs) of 1282 Å³ (Figure 3d) that were filled with disordered





(c)



Figure 3. (a) Molecular structure of the anionic part of complex 1 (thermal ellipsoids are drawn at 40% probability level whereas only phenolic hydrogen atoms are shown for clarity); (b, c) different views of H-bonded networks; (d) space filling model of the packing diagram (view along the c-axis). Hydronium ion has been omitted for clarity in panels b, c, and d. See text for detail.

solvent molecules which could not be assigned and were thus squeezed.

The complex **2** crystallized in the orthorhombic cell and *I*222 space group. As observed for the *p*-phenol isomer (complex 1), in this case also, the intermolecular OH…C=O_{amide} H-bonding was noticed (Figure 4). The *m*-phenolic group O2-H2A forms the O2-H2A···O1^{vi} motif (Figure 4, Table 4) with the C= O_{amide} oxygen atom O1 in a complementary manner. The heteroatom separation between any such interacting pair is 2.610(11) Å, while the O–H…O_amide angle was 164° (Figure 4b; Table 4). Notably, for the *m*-phenol (complex 2), the OH…C=O_{amide} H-bond is ca. 0.08 Å shorter than the *p*-phenol (complex 1). In compound 2, the hydronium ion (which is required to balance the charge) was found to interact with the complex anion. Although the hydrogen atoms of the hydronium ion could not be located but from the short interatomic contacts between O1...O3 (2.78(2) Å) and O3...O3^a (2.89(3) Å, where a = 1 - x, y, -z), it may be inferred that the hydronium ion is involved in H-bonding interactions with the complex anion and its own symmetry related counterpart.

These interactions result in the generation of a chain running in the *ac* plane (shown in purple color; Figure 4c). The purple chain further connects with two alternate chains (green chains from top and bottom without containing the hydronium ions) that result in the generation of a 2D network (Figure 4c). The SAVs are clearly visible in the space filling diagram of complex 2; however, with much smaller volume of 277 Å³ (Figure 4d) than that of complex 1.

The catechol-based building block (complex 3) also crystallized in the orthorhombic cell and I222 space group (Figure 5). Complex 3 has four peripheral catechol units and thus offers eight H-bond donors in OH and four H-bond acceptors in O_{amide} groups. Clearly, there is a mismatch in the number of donors and acceptors. Consequently, two types of intermolecular H-bonds were detected: first between OH and C=O_{amide} groups and second between OH and OH groups (Figure 5b,c). In this complex, the first O-H group of the catechol ring (O2 at meta position) forms an intermolecular Hbond $(OH \cdots C = O_{amide})$ with the C=O_{amide} oxygen atom O1 (O2…O1^{vii}: 2.585(5)Å, Table 4). The O–H…O_{amide} angle was



Figure 4. (a) Molecular structure of the anionic part of complex 2 (thermal ellipsoids are drawn at 40% probability level whereas only phenolic hydrogen atoms are shown for clarity); (b) a view of H-bonded network; (c) a view of H-bonded network including the hydronium ion; (d) space filling model of the packing diagram (view along the *c*-axis whereas the hydronium ion has been omitted for clarity). See text for detail.

found to be 148°. Interestingly, atom O2 (at meta position) also forms an intramolecular H-bond with the para-positioned OH group O3 with O2···O3ⁱ separation of 2.688(5) Å. Further, the second O-H group of the catechol ring (O3 at para position) donates a H-bond to O2 (at meta position) forming an intermolecular H-bond O3-H31-O2viii with the O3-O2viii separation and O-H…O angle being 2.664(5) Å and 163°, respectively (Table 4). Thus, each of the O-H groups of the catechol ring serves both to donate and accept an H-bond. In complex 3, the hydronium ion (i.e., H_3O^+) was found to make an H-bond with the $C=O_{amide}$ group with the heteroatom (O4…O1) separation of 2.86(2) Å (Figure 5c). A similar situation was noted for the complex 2 (vide supra). The space filling model of complex 3 clearly shows cavities (with volume of 371 Å³) which were partially occupied by the hydronium ions (Figure 5d).

There are several noteworthy structural similarities and differences between three deprotected complexes. For example, compounds 2 and 3 have identical space groups and very similar unit cell parameters. Further, both complexes 2 and 3 display a similar interaction of hydronium ion present in the crystal lattice. Thus, these two complexes may be considered as isomorphous in nature.²⁸ The hydronium ion was found to make an H-bond with the O_{amide} atom in both complexes $2~(2.78(2)~\text{\AA})$ and 3~(2.86(2)Å), whereas it was completely uncoordinated in complex 1 $(O \cdots C = O_{amide} \text{ separation } > 4.5 \text{ Å})$. We relate this observation to a similar but little offset self-assembly in complexes 2 and 3, whereas a highly symmetrical selfassembly in complex 1 has restricted the O_{amide} groups to interact with the hydronium ion. This can be understood in terms of relative twisting of the phenol-containing arene rings in complexes 1 and 2. In complex 1, two *p*-phenol rings make an angle of $70.19(2)^{\circ}$ with each other, whereas this angle increases to $84.28(2)^{\circ}$ for two *m*-phenol rings in complex 2. This increase of ca. 14° is significant and tilts the *m*-phenol rings in such a way that the $C=O_{amide}$ groups are nicely positioned to interact with the hydronium ion. Further, the relative twisting of the phenol rings in complex 2 also makes enough room so that the hydronium ions are comfortably accommodated (Figure 4c). A similar situation was observed for the catechol rings in the case of complex 3 (Figure 5c).



Figure 5. (a) Molecular structure of the anionic part of complex 3 (thermal ellipsoids are drawn at 40% probability level, whereas only catechol hydrogen atoms are shown for clarity); (b, c) views of H-bonded network including the hydronium ion; (d) space filling model of the packing diagram (view along the *c*-axis whereas the hydronium ion has been omitted for clarity). See text for detail.

CONCLUSIONS

To summarize, we have shown that the position of the hydroxyl group on the arene ring (para versus meta) is critical in generating an unique supramolecular architecture. Similarly, the number of hydroxyl groups on the arene ring (phenol versus catechol) is equally significant in determining the outcome of the self-assembly. Once, a perfect symmetry and orientation match is achieved, the result is the generation of a highly symmetrical and complementary network as noted in case of *p*phenol complex 1. We also show that a metal ion can induce structural rigidity and thus places the appended functional groups to a fixed conformation which has only been achieved with synthetically challenging rigid organic molecules. Studies are underway to generalize the geometrical role of metal ion and thus orientation of the appended phenol/catechol rings on the self-assembly process and to investigate the self-assembly in the presence of guest molecules having complementary H-bond donors and acceptors.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data for complexes 1^{P} , 3^{P} , and 1-3 in CIF format, figures for absorption spectra; FTIR spectra; NMR

spectra; TGA-DTA analysis; XRPD patterns; and N_2 sorption studies; and a table for hydrogen bonding metrics. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) The pK_a measurements were done by titrating the complexes 1–3 against NaOH in water using a pH meter.

(26) The experimentally observed values of $\nu_{\rm O-H}$ stretches for the deprotected complexes 1–3 suggest that while the strength decreases from 1–3; the extent of H-bonding increases in the following order: 1 > 2 > 3. Interestingly, while complex 2 was crystallographically observed to form stronger intermolecular H-bond with the O_{amide} group than that of complex 1 (cf. crystal structures); complex 3 with catechol group was engaged in both inter- as well as intramolecular H-bonding thus considerably shifting the $\nu_{\rm O-H}$ values to lower energy. In addition, the observed broadness of the $\nu_{\rm O-H}$ stretches in all three cases further prove the presence of H-bonding in the solid state.

(27) The hydronium ion (H_3O^+) is likely to thermally decompose by eliminating a water molecule while leaving H^+ behind that may stay with the complex anion balancing the charge.

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