Synthesis, characterization and self-assembly of Co³⁺ complexes appended with phenol and catechol groups

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MS received 1 April 2014; revised 16 May 2014; accepted 22 May 2014

Abstract. This work presents the syntheses, characterization and hydrogen bonding based self-assembly of Co³⁺ complexes of pyridine-amide based bidentate ligands containing appended phenol and catechol groups. Placement of multiple hydrogen bond donors (phenolic OH and amidic NH groups) and acceptors (O_{amide} groups) in these molecules results in interesting self-assembled architectures.

Keywords. Cobalt; phenol; catechol; crystal structures; H-bonding

1. Introduction

The construction of extended networks from molecular building blocks is of great importance due to their ability to place molecular components at desirable architectural forms.¹ The use of discrete molecular building blocks further controls the speciation and bonding environments within the extended network.¹ In this context, intricately designed organic molecules² as well as coordination compounds containing hydrogen bond (H-bond) sensitive functional groups^{3,4} are important to understand their self-assembly. A considerable amount of work has been done with organic molecules containing phenolic groups.^{5–11} Out of various such compounds, the molecules containing three phenol moieties (*i.e.*, *tris*-phenols) have been particularly studied.^{5a} Such *tris*-phenols form interesting hydrogen-bonded (H-bonded) assemblies and afford inclusion complexes with solvents serving as the guest molecules.¹² Self-assembly of phenolic compounds show that the molecular geometry of such systems and extent of intermolecular H-bonding interactions result in interesting structures.^{5a} In such cases, O–H group of phenol acts as the H-bond donor while oxygen atom of O–H group functions as the H-bond acceptor to generate O–H...O synthon based H-bonded network.^{2a} Although, phenol-based organic molecules show interesting H-bond based self-assembly; multi-step synthesis has limited their wider utilization.^{10,11} As an alternate, a suitable metalloligand can take the advantage of

structural rigidity and has the ability to place appended functional groups to desirable orientations.¹ Utilizing this concept; we have recently shown the self-assembly of Co³⁺-based building blocks appended with phenol and/or catechol³ as well as arylcarboxylic acid groups.⁴ An important aspect of such work was that these complexes offered both H-bond donors (in O–H groups) as well as acceptors (in O_{amide} or O_{acid} groups) in a single molecule and thus operated in a highly complementary manner.^{3,4} We have successfully shown that once position, number, symmetry and orientation are in place; result is the generation of a highly symmetrical and complementary network. Herein, we report cobalt complexes of bidentate ligands containing appended *para*-, *meta*-phenol or catechol groups to understand their hydrogen bonding (H-bonding) based self-assembly. We attempt to delineate the difference(s) introduced for transitions from the metalloligands with tridentate ligands to the ones with bidentate ligands containing appended functional groups.

2. Experimental

2.1 Materials and reagents

Pyridine-2-carboxylic acid (Sigma-Aldrich), 3-methoxy aniline, 4-methoxy aniline, 3,4-methylenedioxy aniline (Spectrochem), and triphenylphosphite (Sigma-Aldrich) were used as received. Solvents were purified as per the standard literature method.¹³ The ligands HL^{p-OMe}, HL^{m-OMe} and HL^{md} were synthesized as per our recent report.¹⁴

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2.2 Physical measurements

The conductivity measurements were done in organic solvents using the digital conductivity bridge from the Popular Traders, India (model number: PT-825). The elemental analysis data were obtained from Elementar Analysensysteme GmbH Vario EL-III instrument. The NMR measurements were done using either an Avance Bruker (300 MHz) or Jeol (400MHz) instrument. The infra-red spectra were recorded using the Perkin Elmer FTIR 2000 spectrometer. The absorption spectra were recorded using the Perkin Elmer *Lambda*-25 spectrophotometer. The mass spectra were obtained either on Jeol SX102/DA-6000 or Waters LC-TOF instruments. The thermal analyses were performed with a Shimadzu DTG-60 instrument in the temperature range of 25–800 °C.

2.3 X-Ray crystallography

Single crystals suitable for the X-ray diffraction studies of complexes **1^P**, **3^P**, **1** and **2** were grown by the vapour diffusion of diethyl ether or isopropyl ether to a DMF 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).^{15,16} The intensity data were corrected for the Lorentz and polarization effects.¹⁶ The multi-scan absorption correction was also

applied.¹⁷ The structures were solved by the direct methods using SIR-97¹⁸ and refined by full-matrix least-squares method on F^2 (SHELXL-97).¹⁹ All calculations were carried out using the WinGX crystallographic package.²⁰ The non-hydrogen atoms were refined anisotropically whereas all hydrogen atoms were fixed geometrically with Uiso values of 1.2, 1.2 and 1.5 times the Uiso values of methylene, phenylene and methyl carbon atoms, respectively. For complex **2**, atoms C29, O5, C30 and N1 were refined isotropically. Further for complex **2**, attempts to refine peaks of residual electron density as guest atoms were unsuccessful, although atoms of solvent molecule (DMF) were observed but could not be modelled satisfactorily during the structure refinement. Therefore data were corrected for disordered electron density by using the SQUEEZE procedure implemented in PLATON.²¹ A total solvent-accessible void volume of 240.0×10^{-3} Å³ with a total electron count of 46 was found in the unit cell. The crystallographic data collection and structure refinement parameters for all complexes are summarized in table 1.

2.4 Synthesis

[Co(L^{P-OMe})₃] (**1^P**). Ligand H₂L^{P-OMe} (0.100 g, 0.43 mmol) was dissolved in DMF and treated with NaH (0.011 g, 0.47 mmol). The mixture was stirred for 10 min. Solid [Co(H₂O)₆](ClO₄)₂ (0.052 g, 0.14 mmol) was added to the above said mixture under magnetic

Table 1. Crystallographic data collection and structure solution parameters for complexes **1^P**, **3^P**, **1** and **2**.

	1^P	3^P	1	2
Molecular formula	C ₃₉ H ₃₃ CoN ₆ O ₇	C ₃₉ H ₂₇ CoN ₆ O ₁₀	C ₃₆ H ₂₈ ClCoN ₆ O ₁₀	C ₃₉ H ₃₅ BrCoN ₇ O ₁₁
Fw	756.64	798.61	799.02	916.58
T(K)	293(2)	293(2)	120(2)	293(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.0395 (4)	10.0867(19)	17.031(2)	15.180(4)
<i>b</i> (Å)	13.0205 (5)	11.094(2)	21.339(3)	16.469(4)
<i>c</i> (Å)	14.7947 (4)	16.217(3)	22.049(3)	17.268(4)
α [°]	98.001(3)	76.363(3)	90	90
β [°]	108.472(4)	78.422(3)	91.190(3)	91.321
γ [°]	105.196(3)	80.208(4)	90	90
<i>V</i> (Å ³)	1717.20(11)	1713.25(18)	8011.3(19)	4316(2)
<i>Z</i>	2	2	8	4
<i>d</i> (g cm ⁻³)	1.463	1.548	1.325	1.408
<i>F</i> (000)	784	820	3280	1864
Goodness of fit (F^2)	1.113	1.104	0.948	0.996
R_1 , wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0368$, $wR_1 = 0.0962$	$R_1 = 0.0897$, $wR_1 = 0.2440$	$R_1 = 0.0737$, $wR_1 = 0.2426$	$R_1 = 0.1076$, $wR_1 = 0.2768$
R_1 , wR_2 [all data]	$R_2 = 0.0473$, $wR_2 = 0.0984$	$R_2 = 0.1218$, $wR_2 = 0.2943$	$R_2 = 0.0987$, $wR_2 = 0.2677$	$R_2 = 0.1641$, $wR_2 = 0.3125$

^a $R_1 = \Sigma \|F_o\|F_c\|/\Sigma |F_o|$; $wR = \{[\Sigma(|F_o|^2|F_c|^2)]^{1/2}\}$.

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 re-dissolved in DMF and subjected to vapour diffusion of diethyl ether. This resulted in a highly crystalline product within a day. Yield: 0.160 g (70%). Anal. Calcd for C₃₉H₃₃CoN₆O₆·2H₂O: C, 60.31; H, 4.80; N, 10.82. found: C, 60.51; H, 4.45; N, 10.95. Conductivity (DMF, ~1 mM solution, 298 K): $\Lambda_M = 6 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. FTIR spectrum (KBr, ν (cm⁻¹)): 3073, 2934, 2834 (C-H), 1622, 1592, 1568 (C=O), 1506 (C=N). Absorption spectrum (DMF, $\lambda_{\text{max}}/\text{nm}$ (ϵ , M⁻¹cm⁻¹): 635 (110), 432 (sh) (610). ¹H NMR (400 MHz, DMSO): δ 3.49, 3.56, 3.67 (s, 9H, OCH₃ protons for three asymmetric ligands), 8.94 (d, $J = 6.4\text{Hz}$, 1H, H₂), 8.59 (d, $J = 6.88\text{Hz}$, 1H, H_{2'}), 8.26 (t, $J = 8\text{Hz}$, 1H, H₄), 8.11 (d, $J = 12.36\text{Hz}$, 1H, H_{2''}), 7.95 (t, $J = 8\text{Hz}$, 1H, H_{4'}), 7.87 (t/m, 1H/1H, H_{4''} & H₃), 7.67 (d, $J = 7.56\text{Hz}$, 1H, H₅), 7.50 (d, $J = 8.04\text{Hz}$, 1H, H_{5'}), 7.40 (t/m, 1H/1H, H₃/H_{3''}), 7.31 (d, $J = 6.84\text{Hz}$, 1H, H_{5''}), 6.80 (d, $J = 10.08\text{Hz}$, 2H, H₁₀H₁₂), 6.69 (d, $J = 7.8\text{Hz}$, 6H, H_{10'}H_{12'}/H_{10''}H_{12''}), 6.44 (d, $J = 8.24\text{Hz}$, 2H, H₉ & H₁₃), 6.23 (d, $J = 9.16\text{Hz}$, 4H, H_{9'} & H_{13'/H9''} & H_{13''}) ppm. ¹³C NMR (100 MHz, DMSO): δ 169.67, 168.98, 168.59 (C₇/C_{7'}/C_{7''} for three asymmetric ligands), 157.38, 156.03, 155.91 (C₆/C_{6'}/C_{6''}), 155.85, 155.74, 155.57 (C₈/C_{8'}/C_{8''}), 149.86, 149.34, 149.17 (C₂/C_{2'}/C_{2''}), 141.08, 139.89, 139.44 (C₁₁/C_{11'}/C_{11''}), 137.62, 137.06 (C₄/C_{4'}), 128.58, 128.29, 127.55, 127.54 (C_{4''}/C₃/C_{3'}/C_{3''}), 125.74, 124.84, 124.21 (C₅/C_{5'}/C_{5''}), 113.80, 113.28, 112.55 (C₉, C₁₀, C₁₂, C₁₃/C_{9'}, C_{10'}, C_{12'}, C_{13'/C9''}, C_{10''}, C_{12''}, C_{13''}), 55.15, 55.13, 55 (-OCH₃ protons for three asymmetric ligands) ppm.

[Co(L^{m-OMe})₃] (**2^P**). This complex was synthesized in a similar manner with identical scale as discussed for complex **1^P**, however using ligand H₂L^{m-OMe}. Yield: 0.155 g (70%). Anal. Calcd for C₃₉H₃₃CoN₆O₆·H₂O: C, 61.93; H, 5.20; N, 10.83. found: C, 61.67; H, 4.84; N, 10.96. Conductivity (DMF, ~1 mM solution, 298 K): $\Lambda_M = 5 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. FTIR spectrum (KBr, ν (cm⁻¹)): 3070, 2930 (C-H), 1622, 1595, 1590 (C=O), 1488 (C=N). Absorption spectrum (DMF, $\lambda_{\text{max}}/\text{nm}$ (ϵ , M⁻¹cm⁻¹): 632 (80), 437 (sh, 565). ¹H NMR (400 MHz, DMSO): δ 3.54, 3.45, 3.42 (s, 9H, OCH₃ protons for three asymmetric ligands), 8.95 (d, $J = 4.6$, 1H, H₂), 8.66 (d, $J = 5.04$, 1H, H_{2'}), 8.30 (t, $J = 7.36\text{Hz}$, 1H, H₄), 8.14 (d, $J = 7.8\text{Hz}$, 1H, H_{2''}), 7.97 (t, $J = 6.88\text{Hz}$, 1H, H_{4'}), 7.88 (m, 1H/1H, H_{4''} & H₅), 7.64 (d, $J = \text{Hz}$, 1H, H_{5'}), 7.55 (d, 1H, H₃), 7.44 (m, 1H/1H,

H_{3'} & H_{3''}), 7.35 (d, $J = 5.52$, 1H, H_{5''}), 7.08 (broad, 1H/1H, H₉ & H_{9'}), 6.80 (m, 1H/1H, H₁₂ & H_{9''}), 6.72 (d, $J = 8.68\text{Hz}$, 1H/1H, H₁₃ & H_{13'}), 6.61 (t, 1H/1H, H_{12'} & H_{12''}), 6.49 (d, $J = 7.32$, 1H/1H, H_{13''} & H₁₁), 6.33 (d, $J = 6.33$, 1H/1H, H_{11'} & H_{11''}) ppm. ¹³C NMR (100 MHz, DMSO): δ 170.29, 169.70, 169.29 (C₇/C_{7'}/C_{7''} for three asymmetric ligands), 157.71, 156.31, 156.12 (C₁₀/C_{10'}/C_{10''}), 150.62, 150.15 (C₂/C_{2''}), 149.82 (C_{5''}), 147.83, 147.11, 146.65 (C₆/C_{6'}/C_{6''}), 144.88, 144.29, 144.07 (C₈/C_{8'}/C_{8''}), 141.67 (C_{2'}), 141.45, 140.62, 140.56 (C₄/C_{4'}/C_{4''}), 139.45 (C₅), 129.44 (C_{5''}), 128.23 (C₁₂/C_{9'}), 126.36, 125.51, 124.88 (C₃/C_{3'}/C_{3''}), 109.26 (C_{12'/C12''}), 108.33 (C₁₃/C_{13'}), 107.99 (C_{13''/C11}), 107.39 (C_{11'}), 101.51 (C_{11''}), 101.34, 101.14 (C₉/C_{9'}) ppm.

[Co(L^{md})₃] (**3^P**). This complex was also synthesized in a similar manner as discussed for complex **1^P**. Yield: 0.164 g (75%). Anal. Calcd for C₃₉H₂₇CoN₆O₉·3H₂O: C, 55.99; H, 3.98; N, 10.04. found: C, 56.25; H, 3.63; N, 10.27. Conductivity (DMF, ~1 mM solution, 298 K): $\Lambda_M = 8 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. FTIR spectrum (KBr, ν (cm⁻¹)): 3067, 2927 (C-H), 1625, 1597 (C=O), 1485 (C=N). Absorption spectrum (DMF, $\lambda_{\text{max}}/\text{nm}$ (ϵ , M⁻¹cm⁻¹): 628 (82), 424 (sh, 490). ¹H NMR (400 MHz, DMSO-d₆): δ 5.78, 5.76, 5.74 (s, 6H, OCH₂ protons for three asymmetric ligands), 8.88 (d, $J = 5.1$, 1H, H₂), 8.58 (d, $J = 5.1$, 1H, H_{2'}), 8.27 (d, $J = 7.2\text{Hz}$, 1H, H₄), 8.11 (d, $J = 5.1\text{Hz}$, 1H, H_{2''}), 8.02 (t, $J = 7.2\text{Hz}$, 1H, H_{4'}), 7.94 (m, 1H/1H, H_{4''} & H₅), 7.74 (d, $J = 7.5\text{Hz}$, 1H, H_{5'}), 7.58 (d, 1H, H_{5''}), 7.44 (m, 1H/1H, H_{3'} & H_{3''}), 7.33 (d, $J = 5.1$, 1H, H_{3''}), 6.69 (d, $J = 8.1$, 1H, H₁₃), 6.43 (d, $J = 8.1$, 1H, H_{13'}), 6.38 (d, $J = 8.1$, 1H, H_{13''}), 6.28 (m, 1H/1H, H₉ & H_{9'}), 5.99 (s, 1H, H_{9''}), 5.86 (d, $J = 9.9\text{Hz}$, 1H/1H, 1H, H₁₂, H_{12'} & H_{12''}) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ 169.74, 169.15, 168.70 (C₇/C_{7'}/C_{7''} for three asymmetric ligands), 157.19, 155.80, 155.61 (C₆/C_{6'}/C_{6''}), 150.06, 149.60, 149.28 (C₂/C_{2'}/C_{2''}), 147.29, 146.56, 146.11 (C₁₀/C_{10'}/C_{10''}), 144.33, 143.75, 143.52 (C₁₁/C_{11'}/C_{11''}), 141.11, 140.94 (C₄/C_{4'}), 140.06 (C_{4''/C8}), 138.93, 138.35 (C_{8'/C8''}), 128.87 (C₃/C_{3'}), 127.67 (C_{3''/C5/C5'}), 125.80 (C_{5''/C13}), 124.94 (C_{13'/13''}), 120.58, 120.18 (C₁₂/C_{12'}), 108.73 (C_{12''}), 107.79, 107.44, 106.83 (C₉/C_{9'}/C_{9''}), 100.96, 100.79, 100.59 (-OCH₂ carbons for three asymmetric ligands) ppm.

[Co(L^{P-OH})₃]ClO₄ (**1**). Complex **1^P** (0.5 g, 0.67 mmol) was dissolved in 40 mL dry and degassed CH₂Cl₂ and BBr₃ (0.25 mL, 2.02 mmol) was introduced to the solution under a nitrogen atmosphere at -70 °C. The resulting reddish-brown slurry was stirred for 4 h. The slurry was slowly quenched by the addition of MeOH. Evaporation of the solvent provided a brown solid which was crystallized from methanol containing NaClO₄. Yield: (0.25 g, 55%). Anal. Calcd

for $\text{C}_{37}\text{H}_{32}\text{CoN}_6\text{O}_6\cdot\text{ClO}_4\cdot 3\text{H}_2\text{O}\cdot\text{CH}_3\text{OH}$: C, 50.70; H, 4.59; N, 9.34. Found: C, 51.22; H, 4.35; N, 9.62. Conductivity (DMF, ~ 1 mM solution, 298 K): $\Lambda_{\text{M}} = 68 \text{ } \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. FTIR spectrum (KBr, ν (cm^{-1})): 3344 (NH), 3342 (OH), 1654, 1603 (C=O), 1511 (C=N). Absorption spectrum (DMF, $\lambda_{\text{max}}/\text{nm}$ (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 634 (105), 447 (820), 312 (sh, 1420). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.01 (dd, $J = 12.84\text{Hz}$, 2H, H_2 & $\text{H}_{2'}$), 8.54 (t, $J = 9.16\text{Hz}$, 1H, H_4), 8.15 (t, $J = 6.88\text{Hz}$, 1H, $\text{H}_{4'}$), 7.97 (m, 4H, $\text{H}_{2''}$, $\text{H}_{4''}$, H_3 , H_5), 7.75 (d, $J = 8.28\text{Hz}$, 1H, $\text{H}_{5'}$), 7.66 (d, $J = 9.16\text{Hz}$, 1H, $\text{H}_{5''}$), 7.46 (d, $J = 10.96\text{Hz}$, 2H, H_9 & H_{13}), 7.32 (m, 2H, $\text{H}_{3'}$ & $\text{H}_{3''}$), 6.81 (d, $J = 8.24\text{Hz}$, 6H, H_9 , $\text{H}_{13'}$ / $\text{H}_{9''}$, $\text{H}_{13''}$ / H_{10} , H_{12}), 6.28 (d, $J = 14.68\text{Hz}$, 4H, $\text{H}_{10'}$, $\text{H}_{12'}$ / $\text{H}_{10''}$, $\text{H}_{12''}$), 12.23 (s, 1H, NH), 9.87 (s, 2H, OH), 9.19 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 169.88, 168.97, 168.24 ($\text{C}_7/\text{C}_{7'}/\text{C}_{7''}$ for three asymmetric ligands), 156.68, 156.28 (C_6 , $\text{C}_{6'}$), 154.85, 154.62, 154.08 ($\text{C}_{6''}$, C_8 , $\text{C}_{8'}$), 151.50, 150.42 (C_2 , $\text{C}_{2'}$), 149.39, 149.13 ($\text{C}_{2''}$, $\text{C}_{8''}$), 141.82 (C_3), 140.52 (C_4), 136.20 (C_{11}), 135.19 ($\text{C}_{11'}$), 131.93 ($\text{C}_{4'}$), 128.93 ($\text{C}_{4''}$), 128.09 (C_3), 127.18 ($\text{C}_{3'}$), 126.58 ($\text{C}_{11''}$), 125.01 (C_5), 124.56 ($\text{C}_{5'}$), 124 (C_9 , $\text{C}_{13'}$ / C_9 , $\text{C}_{13''}$ / C_9'' , $\text{C}_{13''}$), 115.48 (C_{10} , $\text{C}_{12'}$ / $\text{C}_{10'}$, $\text{C}_{12''}$ / $\text{C}_{10''}$, $\text{C}_{12''}$) 115.21 ($\text{C}_{5''}$) ppm.

$[\text{Co}(\text{L}^{\text{m-OH}})_3]\text{Br}$ (**2**). This complex was synthesized in a similar manner with an identical scale as discussed for complex **1**. Yield: (0.22 g, 50%). Anal. Calcd for $(\text{C}_{37}\text{H}_{32}\text{CoN}_6\text{O}_6\cdot\text{Br}\cdot 3\text{H}_2\text{O})$ C, 52.37; H, 4.39; N, 9.90. found: C, 52.15; H, 4.05; N, 10.25. Conductivity (DMF, ~ 1 mM solution, 298 K): $\Lambda_{\text{M}} = 75 \text{ } \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. FTIR spectrum (KBr, ν (cm^{-1})): 3358 (NH), 3360 (OH), 1664, 1603 (C=O), 1540 (C=N). Absorption spectrum (DMF, $\lambda_{\text{max}}/\text{nm}$ (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) (DMF): 638 (130), 423 (sh, 810), 303 (sh, 940). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.05 (d, $J = 7.8\text{Hz}$, 1H, H_2), 8.96 (d, 1H, $\text{H}_{2'}$), 8.59 (t, $J = 7.76\text{Hz}$, 1H, H_3), 8.20 (t, $J = 6.2\text{Hz}$, 1H, $\text{H}_{3'}$), 7.98 (m, 1H/1H/1H, $\text{H}_{3''}$, H_5 , $\text{H}_{2''}$), 7.77 (d, $J = 7.32\text{Hz}$, 1H, $\text{H}_{5'}$), 7.66 (d, $J = 6.88$, 1H, $\text{H}_{5''}$), 7.32 (s, 1H/1H/1H, H_9 , $\text{H}_{9'}$, $\text{H}_{9''}$) 7.25 (t, $J = 8.26$, 1H/1H/1H, H_4 , $\text{H}_{4'}$, $\text{H}_{4''}$), 7.14 (d, $J = 6.88$, 1H, H_{13}), 7.06 (d, 1H, $\text{H}_{13'}$), 6.73 (d, $J = 6.4$, 1H, $\text{H}_{13''}$), 6.65 (t, 1H/1H, H_{12} , $\text{H}_{12'}$), 6.39 (t, 1H, $\text{H}_{12''}$), 6.37 (d, 1H/1H/1H, H_{11} , $\text{H}_{11'}$, $\text{H}_{11''}$) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 169.94, 169.86, 168.98 ($\text{C}_7/\text{C}_{7'}/\text{C}_{7''}$ for three asymmetric ligands), 158.37, 157.83, 157.34 ($\text{C}_{10}/\text{C}_{10'}/\text{C}_{10''}$), 154.55, 151.93, 151.65 ($\text{C}_6/\text{C}_{6'}/\text{C}_{6''}$), 150.06, 149.57 ($\text{C}_2/\text{C}_{2'}$), 146.60, 145.60 ($\text{C}_8/\text{C}_{8'}$), 142.49 ($\text{C}_3/\text{C}_{3'}$), 141.23 (C_2/C_5), 136.62 ($\text{C}_{8''}$), 132.64 ($\text{C}_4/\text{C}_{4'}/\text{C}_{4''}$), 130.43 ($\text{C}_9/\text{C}_9'/\text{C}_{9''}$), 129.46 ($\text{C}_{12}/\text{C}_{12'}$), 128.60 ($\text{C}_{2'}$), 128.40 ($\text{C}_{3'}$), 125.53 ($\text{C}_{5'}$), 125.15 ($\text{C}_{5''}$), 115.61 ($\text{C}_{13''}$), 115.14 ($\text{C}_{11}/\text{C}_{11'}/\text{C}_{11''}$), 113.44 ($\text{C}_{12''}$), 113.09 (C_{13}), 110.08 ($\text{C}_{13'}$) ppm.

$[\text{Co}(\text{L}^{\text{cat}})_3]\text{Br}$ (**3**). The complex **3** was also synthesized in a similar manner as discussed for complex **1**. Yield: (0.26 g, 55%). Anal. Calcd. for $\text{C}_{37}\text{H}_{32}\text{CoN}_6\text{O}_{13}\cdot\text{Br}\cdot 2\text{H}_2\text{O}$: C, 50.58; H, 4.02; N, 9.57. Found: C, 51.10; H, 3.92; N, 9.82. Conductivity (DMF, ~ 1 mM solution, 298 K): $\Lambda_{\text{M}} = 82 \text{ } \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. FTIR spectrum (KBr, ν (cm^{-1})): 3413 (NH), 3378 (OH), 1590, 1563 (C=O), 1481 (C=N). Absorption spectrum (DMF, $\lambda_{\text{max}}/\text{nm}$ (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 645 (160), 450 (sh, 620), 317 (sh, 1200). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.54 (d, 1H, $\text{H}_{2'}$), 8.41 (d, 1H, $\text{H}_{2''}$), 8.32 (d, 1H, H_2), 8.24 (d, $J = 7.8\text{Hz}$, 1H/1H, $\text{H}_{5'}/\text{H}_{5''}$), 8.20 (d, 1H/1H, H_4 , $\text{H}_{4''}$), 7.83 (m, 1H, H_4), 7.81 (d, $J = 7.8$, 1H/1H, $\text{H}_{3'}$, $\text{H}_{3''}$), 7.41 (dd, 1H/1H, H_5 , H_3) 6.18 (d, $J = 2.28$, 1H/1H, $\text{H}_{13'}$, $\text{H}_{13''}$), 6.15 (dd, $J = 8.28\text{Hz}$, 1H/1H, $\text{H}_9/\text{H}_{9''}$), 6.10 (dd, $J = 8.28\text{Hz}$, 1H/1H, $\text{H}_{12'}/\text{H}_{12''}$), 5.86 (dd, $J = 4.12\text{Hz}$, 1H/1H, H_{12} , H_{13}), 5.83 (dd, 1H, H_9), 9.15 (s, $-\text{OH}$), 9.31 (s, $-\text{OH}$), 11.59 (s, $-\text{NH}$) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 166.56 ($\text{C}_7/\text{C}_{7''}$ for three asymmetric ligands), 165.52 (C_7), 157.11 ($\text{C}_6/\text{C}_{10'}$), 156.66 ($\text{C}_{2'}/\text{C}_{2''}$), 156.62 ($\text{C}_{10''}$), 151.13 ($\text{C}_{6'}$), 151.11 ($\text{C}_{6''}$), 145.20 ($\text{C}_{8'}$), 145.19 ($\text{C}_{8''}$), 143.98 ($\text{C}_2/\text{C}_4/\text{C}_{4'}/\text{C}_{4''}$), 142.44 (C_8), 141.82 ($\text{C}_{11'}/\text{C}_{11''}$), 141.01 ($\text{C}_{3'}/\text{C}_{3''}/\text{C}_5/\text{C}_9$), 137.88 ($\text{C}_{13'}/\text{C}_5/\text{C}_{5''}$), 137.14 ($\text{C}_{10'}$), 134.80 (C_{11}), 122.04 ($\text{C}_3/\text{C}_{12'}$), 116.32 ($\text{C}_{12''}/\text{C}_{13''}$), 114.32 ($\text{C}_9'/\text{C}_{13}$), 114.01 (C_9/C_{12}) ppm.

3. Results and Discussion

3.1 Synthesis and characterization of protected ($\text{I}^{\text{P}}\text{-3}^{\text{P}}$) and deprotected complexes (**1-3**)

The Co^{3+} complexes $\text{I}^{\text{P}}\text{-3}^{\text{P}}$ containing protected phenol and catechol groups were synthesized by treating the respective ligand with NaH, followed by the addition of $[\text{Co}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$. The subsequent deprotection with BBr_3 provides complexes **1-3** with free phenol and catechol groups.³ Interestingly, during deprotection; one of the bidentate ligands was protonated and coordinated via neutral O_{amide} atom with intact N-H group (scheme 1). We believe that the generation of HBr changes pH of the reaction medium in such a way that only one of the ligands is protonated. Further, additional protonation is likely to produce highly charged species that may not be stable. As a result, complexes **1-3** are mono-cationic in nature and the charge is balanced by ClO_4^- in **1** whereas by Br^- in **2** and **3**. The source of bromide ion was the generation of HBr during the deprotection step whereas NaClO_4 was added to facilitate crystallization in case of complex **1**. The solution molar conductivity data²² confirmed 1:1 electrolytic nature for deprotected complexes **1-3**. On the other hand,

Scheme 1. Schematic representation for the synthesis of complexes **1^P–3^P** and **1–3**. Conditions: (i) 1 equiv. NaH, DMF, N₂; (ii) 1/3 equiv. [Co(H₂O)₆](ClO₄)₄; (iii) excess O₂; (iv) BBr₃, CH₂Cl₂.

protected complexes **1^P–3^P** were neutral in nature. The microanalytical data supported the proposed formulation and purity of the bulk sample for all six complexes. The absorption spectra of protected (**1^P–3^P**) and deprotected (**1–3**) were measured in DMF solution (figures S1 and S2). All complexes are red-brown in colour and display λ_{max} in a close range of 632–645 nm that is assigned to d-d transitions.^{3,4} The high-energy features observed between 432–450 nm and those below 430 nm could tentatively be assigned as the ligand-to-metal charge transfer and intra-ligand transitions, respectively.^{3,4} The absence of $\nu_{\text{N-H}}$ stretches and red-shifted C=O_{amide} stretches in the FTIR spectra of complexes **1^P–3^P** suggests deprotonated form of the ligands. Notably, C=O_{amide} stretches were observed at three distinct positions justifying the asymmetry of all three coordinated ligands due to the meridional geometry around the Co(III) ion.^{23,24} The deprotected complexes **1–3** contain one protonated ligand as confirmed by the observation of sharp $\nu_{\text{N-H}}$ stretches. These complexes also show $\nu_{\text{O-H}}$ stretches as broad feature between 3344–3413 cm⁻¹. The observed broadness for the phenol/catechol group points toward the presence of H-bonding in these complexes (cf. Crystal Structures).

To understand the thermal stability and decomposition profile of complexes **1–3** with free phenol and catechol groups, their thermogravimetric analysis (TGA) were performed (figures S3). All three complexes were found to crystallize with a certain number of solvent molecules and the TGA profiles perfectly displayed

their elimination between 50–200 °C. For example, complex **1** shows 9.2% weight change (calcd. 9.6%) for the loss of one methanol and three water molecules. Similarly, complexes **2** (obs. 6.0%; calcd. 6.4%) and **3** (obs. 3.8%; calcd. 4.1%) exhibit weight loss due to three and two water molecules, respectively. The presence of solvate molecules in all three complexes was further supported from the microanalytical results.

3.2 NMR Spectral Studies

The diamagnetic nature for all cobalt complexes has helped us in characterizing them by ¹H and ¹³C NMR spectra (figures S4–S13 and tables S1–S6). The NMR spectra of the protected (**1^P–3^P**) and deprotected (**1–3**) complexes are quite complex yet interesting. The meridional (*mer*) geometry around the Co(III) ion has caused asymmetry to all three coordinated ligands.^{23,24} The effect of this asymmetry is clearly visible in the form of 3-fold signals in the proton as well as carbon NMR spectra. For example, any of the coordinated ligand is expected to display either eight (for *para*- or *meta*-phenol) or seven (for catechol) ring-proton signals due to two chemically different arene rings. However, 24 (for *para*- or *meta*-phenol) and 21 (for catechol) proton signals were observed. All quaternary carbon atoms were assigned with the help of DEPT NMR spectrum whereas 2D {¹H-¹³C} correlation spectra were used for the correct assignment of various resonances. The NMR spectra of complexes **1^P** and **1** have been discussed as the representative examples while a somewhat similar observation was noted for the remaining complexes **2^P/2** and **3^P/3**. The proton NMR spectrum of complex **1^P** shows 24 signals in the aromatic region due to three asymmetrical ligands each having eight chemically different protons. In addition, three singlet resonances were observed at 3.49, 3.56 and 3.67 ppm for the –OMe protons. Similarly, ¹³C NMR spectrum of complex **1^P** displays 36 signals for three asymmetrical ligands each having twelve unique ring-carbon centres. In addition, three signals were observed for the –OMe carbon atoms at 55.13, 55.15 and 55.21 ppm. The ¹H and ¹³C NMR spectra of complex **1** were quite similar to that of complex **1^P** except that the methoxy signals were disappeared whereas all aromatic signals were slightly shifted. As explained earlier, deprotected complexes contain one of the ligands in its protonated form. As a result, complex **1** displays –NH proton at 12.23 ppm whereas phenolic OH protons were appeared at 9.87 (broad, two H) and 9.19 (one H) ppm. The remaining ring-protons were observed between 6–9 ppm as multiplets.

3.3 Crystal structure studies

Two protected and two deprotected complexes were structurally characterized to evaluate their molecular structures and to understand their self-assembly via H-bonding interactions. The selected bond distances and bond angles of all complexes have been presented in tables 2 and 3 whereas H-bonding parameters are listed in table 4.

3.3a Crystal structures of 1^P and 3^P : The molecular structures of protected complexes $[\text{Co}(\text{L}^{\text{P-OMe}})_3]\cdot\text{H}_2\text{O}$ (1^P) and $[\text{Co}(\text{L}^{\text{md}})_3]\cdot\text{H}_2\text{O}$ (3^P) are quite similar and both of them crystallized in the triclinic cell system with *P*-1 space group. Both complexes differ by the peripheral substituents; methoxy in 1^P and methylenedioxy groups in 3^P (figure 1). In both complexes, three deprotonated bidentate ligands are arranged octahedrally around the Co^{3+} ion via five-membered chelate rings between N_{amide} and $\text{N}_{\text{pyridine}}$ atoms. The $\text{Co}(\text{III})$ ion is thus sitting in an N_6 -coordination sphere and is a little distorted from the ideal octahedral geometry. For both complexes, average $\text{Co-N}_{\text{amide}}$ and $\text{Co-N}_{\text{pyridine}}$ bond distances are comparable, therefore indicating a symmetrical bonding from all donors.²⁴ All diagonal angles are more or less *trans* in nature, ranging from 173.2° to 176.5° for 1^P and 174.9° to 176.2° for 3^P . This observation further suggests a symmetrical arrangement of donors resulting in a nearly octahedral geometry. The

Table 2. Selected bond distances [$\text{\AA}$] and angles [$^\circ$] for complexes 1^P and 3^P .

Complexes	1^P	3^P
Co-N1	1.955(16)	1.938(6)
Co-N2	1.985(16)	1.972(6)
Co-N3	1.930(16)	1.959(5)
Co-N4	1.927(16)	1.952(6)
Co-N5	1.928(16)	1.946(5)
Co-N6	1.941(16)	1.964(6)
N4-Co-N5	92.63(7)	92.3(2)
N4-Co-N3	82.75(7)	82.8(2)
N5-Co-N3	173.21(7)	174.9(2)
N4-Co-N6	89.45(7)	88.8(2)
N5-Co-N6	82.96(7)	83.2(2)
N3-Co-N6	91.99(6)	93.4(2)
N4-Co-N1	176.54(7)	176.2(2)
N5-Co-N1	89.33(6)	85.4(2)
N3-Co-N1	95.54(6)	94.6(2)
N6-Co-N1	93.61(6)	94.3(2)
N4-Co-N2	95.41(7)	95.0(2)
N5-Co-N2	97.30(6)	98.2(2)
N3-Co-N2	88.12(7)	88.8(2)
N6-Co-N2	175.11(6)	175.0(2)
N1-Co-N2	81.51(6)	82.02(2)

Table 3. Selected bond distances [$\text{\AA}$] and angles [$^\circ$] for complexes **1** and **2**.

Complexes	1	2
Co-O1	1.920(4)	1.929(8)
Co-N1	1.976(4)	1.985(9)
Co-N3	1.921(5)	1.943(8)
Co-N4	1.911(4)	1.888(9)
Co-N5	1.922(5)	1.903(9)
Co-N6	1.924(5)	1.897(9)
N4 Co1 O1	87.26(18)	92.4(4)
N4 Co1 N3	83.14(19)	82.7(4)
O1 Co1 N3	88.13(17)	90.9(3)
N4 Co1 N5	93.99(19)	94.8(4)
O1 Co1 N5	95.90(18)	92.7(4)
N3 Co1 N5	174.95(19)	175.7(4)
N4 Co1 N6	91.03(19)	90.7(4)
O1 Co1 N6	178.05(17)	175.1(4)
N3 Co1 N6	92.60(19)	93.2(4)
N5 Co1 N6	83.27(19)	83.3(4)
N4 Co1 N1	169.34(19)	173.0(4)
O1 Co1 N1	82.30(17)	81.3(4)
N3 Co1 N1	94.33(18)	94.1(4)
N5 Co1 N1	89.23(18)	88.8(4)
N6 Co1 N1	99.44(19)	95.7(4)

five-membered chelate rings showed significant reduction of the bond angles from 90° thus indicating a tight chelation. The planes comprising all three N_{amide} atoms and all three $\text{N}_{\text{pyridine}}$ atoms make an angle of ca. 85° for 1^P and ca. 83° for 3^P with each other, respectively. The relative disposition of all three pyridine and amide donors shows that the complexes have *mer* stereochemistry, which is common in tris-chelated $\text{Co}(\text{III})$ complexes.²⁵ The occurrence of *mer* geometry in 1^P and 3^P has made all three coordinated ligands asymmetrical to each other and that has resulted in the observation of three-fold resonances in the FTIR as well as NMR spectra (vide supra).^{23,24}

Complex 1^P shows various kinds of weak interactions. Two individual molecules are interconnected via $\text{CH}\cdots\text{O}$ interaction involving O1_{amide} atom and methoxy-H atom (C39-H). The heteroatom separation between O1 and C39 was found to be $3.501\text{ \AA}$. Such a pair is further connected to another pair through two types of intermolecular $\text{CH}\cdots\text{O}$ interactions to form a tetramer as shown in figure 2a. The first one is a weak H-bond involving $\text{O}_{\text{methoxy}}$ atoms O2 and O4 as the acceptors and C38-H and C9-H as the donors. The second one is a bifurcated H-bond involving O5_{amide} as acceptor and C15-H and C2-H as the donors. Each tetramer is surrounded by four neighbour tetramers connecting together via three types of $\text{C-H}\cdots\text{O}$ interactions (C3-H $\cdots$ O4, C32-H $\cdots$ O3 and C26-H $\cdots$ O1) with heteroatom separations being 3.331 ,

Table 4. Some important H-bond parameters for complexes **1** and **2**.

Complex	D-H...A	$d(\text{D}\cdots\text{A})/\text{\AA}$	$\angle(\text{DHA})/^\circ$
[Co(L ^p -OH) ₃](ClO ₄) (1)	O(7)-H7a...O(4) ⁽ⁱ⁾	2.657(5)	138.05(29)
	N(7)-H7...O(3) ⁽ⁱⁱ⁾	2.763(5)	155.32(28)
	O(1)-H1b...O(9) ⁽ⁱⁱⁱ⁾	2.611(6)	130.50(29)
	N(1)-H1a...O(12) ^(iv)	2.731(5)	151.25(28)
[Co(L ^m -OH) ₃]Br (2)	O(4)-H40...O(5) ^(v)	2.644(7)	161.49(41)
	N(2)-H2...O(3) ^(vi)	2.821(8)	160.80(42)
	O(6)-H6a...Br ⁽ⁱ⁾	3.175 (8)	175.55(55)

Symmetry transformation used to generate equivalent atoms (i) x, y, z ; (ii) $x, -y+1/2, +z+1/2$; (iii) $x-1, y, z$; (iv) $-x+2, -y+1, -z$; (v) $x-1, -y+1/2, z-1/2$; (vi) $-x+1, -y, -z+2$; (vi) $-x+1/2, y+1/2, -z+1/2+1$.

3.241 and 3.120 Å, respectively. Such a bonding pattern is repeated to generate a 2D network (figure 2c).

Complex **3^p** also shows interesting packing behaviour through weak interactions. A molecule on one side is connected to another molecule via two complementary C-H...O interactions involving O3_{amide} and C13-H and on the other side it is connected to another molecule via a pair of C-H...O interactions involving O1 and C39-H atoms to generate a zigzag chain as shown in figure 3a. The heteroatom separation between C13...O3 and C39...O1 were found to be 3.266 and 3.270 Å, respectively. Two such chains are interconnected via dual C-H...O interactions resulting in a double chain (figure 3b). For the first one, methylenedioxy atoms O5, O6, O7, O8 and O9 are connected with aromatic C24-H, C39-H, C38-H, C24-H and C2-H, hydrogen atoms respectively. For the second one, the interaction is between O2_{amide} and aliphatic-H atom C15-H.

3.3b Crystal structures of 1 and 2: The deprotected complexes **1** and **2** were structurally characterized while complex **3** did not produce suitable crystals for the diffraction studies. Both complexes **1** and **2** crystallized in the monoclinic cell system with $P2_1/n$ and $P2_1/c$ space groups, respectively. The crystal structures display that the central Co(III) ion is coordinated to three N_{pyridine}, two N_{amide} and one O_{amide} atoms maintaining an octahedral geometry (figure 4). This is in contrast to the structures of **1^p** and **3^p** where a Co(III) ion was coordinated to three N_{pyridine} and three N_{amide} atoms. Such a structural difference is due to flipping of one of the bidentate ligands due to protonation of amidic nitrogen during the deprotection step. Both complexes have similar arrangement of ligands around the Co(III) ion with only difference about the position of peripheral OH groups; *para* in **1** and *meta* in **2**. The mono-cationic charge on complexes **1** and **2** was balanced with perchlorate and bromide ions, respectively.

Figure 1. Molecular structure of complex **1^p** (left) and **3^p** (right) with partial numbering scheme. Only methoxy and methylenedioxy hydrogen atoms are shown for clarity.

Figure 2. Packing diagram of complex **1^P** in a view along *b*-axis showing 2D network via C-H...O H-bonding interactions.

The average Co-N_{amide}, Co-N_{pyridine}, and Co-O_{amide} bond distances are quite comparable in complexes **1** and **2**. For both complexes, the planes comprising two N_{amide} atoms along with one O_{amide} to that of three N_{pyridine} atoms make an angle of ca. 85° whereas relative disposition of donor atoms show the occurrence of *mer* stereochemistry. Interestingly, protonation of one of the bidentate ligands has not caused any change in the metal stereochemistry.

As anticipated, both complexes **1** and **2** show several interesting H-bonding interactions. Both complexes contain three phenolic -OH groups and one amidic -NH group in addition to two O_{amide} groups. Therefore, both **1** and **2** offer four H-bond donors (-NH and -OH groups) and two H-bond acceptors (O_{amide} groups). In the crystal structure of **1**, only two OH and one NH groups are involved in H-bonding to that of O_{amide} atoms from the neighbouring molecules (figure 5a). Notably, the unit cell contains two different molecules (shown in blue and green color, respectively) that are connected via H-bond between O7H and O4_{amide} atoms (figure 5b). The heteroatom separation for O7-H...O4 synthon was 2.657(5) Å. Furthermore, packing of complex **1** shows an orderly arrangement wherein a central molecule (shown in green colour) is simultaneously

interacting with four neighbouring molecules (shown in blue colour) via two types of intermolecular H-bonding (figure 5c). The first one is between OH and O_{amide} groups while the second one is between NH and O_{amide} atoms. The heteroatom separations for O1-H...O9 and N7-H...O3 synthons were 2.611(6) and 2.763(5) Å, respectively (table 4). Notably, if the crystal structure of protected complex **1^P** is compared with its de-protected complex **1**; it was observed that the latter generates a highly organized self-assembled network due to the operation of a directional and complementary H-bonding between O-H and O_{amide} synthons. Interestingly, absence of such a complementary O-H...O_{amide} synthon in **1^P** creates the opportunities for the emergence of C-H...OCH₃ as well as C-H...O_{amide} H-bonding interactions.

For complex **2**, NH group and only one of the OH groups (O4) are involved in H-bonding to the neighbouring molecules whereas the remaining OH groups (O6 and O2) are weakly interacting to bromide ion and DMF molecule, respectively (figure 6a). As a result, a central molecule (shown in mustard yellow and highlighted with a peach background) is H-bonded to three neighbouring molecules (two are shown in blue and one in mustard yellow) via OH...O_{amide} and NH...O_{amide}

Figure 3. Packing diagram of complex **3^P** in a view along *c*-axis showing the formation of double chain via C-H...O H-bonding interactions.

synthons (figure 6b). In the resultant network, any two molecules (shown in mustard yellow) are connected via complementary O4-H...O5 H-bonding to create a dimer whereas each dimer is connected to four adjacent dimers through N2-H...O3 H-bonding interactions.

Such a bonding pattern is repeated to generate a 2D network (figure 6c). A The heteroatom separation and bond angle for O4-H...O5 and N2-H...O3 synthons were 2.644 Å and ca. 162°; and 2.821 Å and ca. 161°, respectively.

Figure 4. Molecular structure of the cationic part of complex **1** (left) and **2** (right) with partial numbering scheme. Only phenol and amide hydrogen atoms are shown for clarity.

Figure 5. (a) Chemical drawing of cationic part of complex **1** depicting the functional groups involved in H-bonding (b) A view of two independent molecules within the unit cell connected through a H-bond. (c) Packing diagram of **1** in a view along *b*-axis showing 2D network via assorted H-bonding interactions. Anion has not been shown in (b) and (c).

3.4 Bis-chelated versus tris-chelated Co^{3+} complexes

Our earlier Co^{3+} complexes, **4–6**, of tridentate ligands appended with phenol and catechol functional groups showed the generation of highly symmetrical and complementary H-bonding networks (scheme 2).³ Complexes **4** and **5** offered four phenol H-bond donors in addition to a matching number of O_{amide} acceptors in a complementary fashion which effectively formed a symmetrical array of $[4 \times 4]$ architecture. Interestingly, complex **4** with *para*-phenol substituents afforded a much more symmetrical H-bonded network than that of complex **5** with *meta*-phenol groups. Complex **6** with catechol groups, on the other hand, produced a less symmetrical H-bonded network due to mismatch in the number of H-bond donors (eight $-\text{OH}$ groups) and acceptors (four O_{amide} groups). Such structural observations unambiguously demonstrated the importance of spatial and geometrical placement of H-bond sensitive

functional groups on a metalloligand. In contrast, present complexes, **1–3**, offer three phenol and/or catechol groups in a non-symmetrical manner due to the *mer* geometry at Co(III) centre. Further, the situation becomes more complex due to the presence of N-H group after flipping of one of the ligands as a result of protonation. Furthermore, protonation induces a cationic charge and therefore presence of an anion additionally provides H-bonding possibilities. As a result, the network generation through H-bonding no longer remains either complementary or symmetrical. Unfortunately, complex **3** did not produce diffraction-quality single crystals, therefore, depriving us in evaluating its ability to generate H-bonding network. However, a comparative study of FTIR spectra of all three complexes, **1–3**, indeed displays a similar observation of broad stretches for the O-H groups of the catechol group. Thus, in absence of crystal structure, it could be inferred that complex **3** also forms H-bonded network.

Figure 6. (a) Chemical drawing of cationic part of complex **2** depicting the functional groups involved in H-bonding. (b) Interaction of a molecule (shown in mustard yellow colour and highlighted with a peach background) with its adjacent molecules (in mustard yellow and blue colour), bromide ion (purple ball) and solvent DMF (red colour). (c) Packing diagram of complex **2** in a view along *a*-axis showing 2D network via assorted H-bonding interactions. Anion has not been shown in (c).

Scheme 2. Schematic representations of complexes **4** - **6** with tridentate ligands

4. Conclusion

Bidentate pyridine-amide based ligands containing protected phenol and catechol groups were utilized to synthesize Co^{3+} complexes **1^P**–**3^P**. These complexes on deprotection afforded complexes **1**–**3** with appended phenol and catechol groups. Notably, one of the bidentate ligands was protonated during the deprotection and subsequently coordinated via $\text{N}_{\text{pyridine}}$ and O_{amide} groups. Both complexes **1** and **2** are structural isomers and self-assembled into interesting supramolecular networks. The self-assembly took place via intermolecular $\text{OH} \cdots \text{O}_{\text{amide}}$ and $\text{NH} \cdots \text{O}_{\text{amide}}$

H-bonding synthons and generated two-dimensional sheet-like networks.

Supplementary Information

Figures for absorption spectra, NMR spectra and thermal analysis; and tables for NMR spectra data. The electronic supplementary information can be seen at www.ias.ac.in/chemsci. CCDC 994231–994234 contain the crystallographic data for this paper. These data can be obtained free of charges from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Authors thank Science and Engineering Research Board (SERB), Govt. of India for the generous financial support and CIF-USIC of this university for the instrumental facilities. AA and DB thank University Grant Commission (UGC) for their fellowships.

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