

Supporting information

A Solid-State Valence Tautomeric Octahedral $\{\text{Co}^{\text{II}}[(\text{BQ-N-Cat})]_2\}^0$ Complex Formation *via* Ligand-Centered Phenolic C-O Bond breaking and Co-O Bond making

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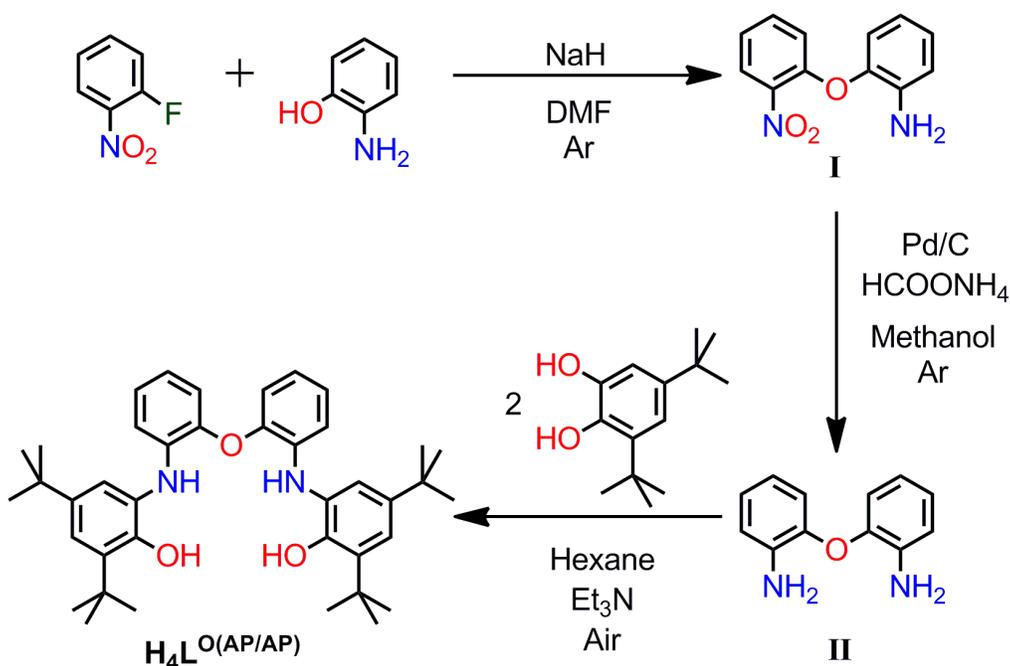
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Contents	Page
Materials and Physical Methods	S3
Synthesis of ligand $\text{H}_4\text{L}^{\text{S(AP/AP)}}$	S4-S5
Synthesis of complex 1 from ligand $\text{H}_4\text{L}^{\text{S(AP/AP)}}$	S6
Figure S1: IR spectrum of ligand $\text{H}_4\text{L}^{\text{O(AP/AP)}}$	S7
Figure S2: ESI–mass spectrum of ligand $\text{H}_4\text{L}^{\text{O(AP/AP)}}$	S7
Figure S3: ^1H NMR spectrum of ligand $\text{H}_4\text{L}^{\text{O(AP/AP)}}$	S8
Figure S4: ^{13}C NMR spectrum of ligand $\text{H}_4\text{L}^{\text{O(AP/AP)}}$	S8
Figure S5: IR Spectrum of complex 1 •0.3CHCl ₃	S9
Figure S6: ESI–mass spectrum of complex 1 •0.3CHCl ₃	S9
Proposed mechanism of the formation of complex 1 from $\text{H}_4\text{L}^{\text{O(AP/AP)}}$	S10
Figure S7: Characterization data for intermediate A	S11
Figure S8: Molecular structure of ligand $\text{H}_4\text{L}^{\text{O(AP/AP)}}$ and the Co complexes	S12
Figure S9: Crystal packing diagram of complex 1 •1CHCl ₃	S13
Figure S10: Crystal packing diagram of complex 1 •1CH ₃ CN	S14
Figure S11: Temperature dependent UV-Vis spectra of complex 1 in toluene	S15
Table S1: Selected bond distances (Å) for the Co complexes	S15
Table S2: Crystallographic data and its quality-limitations (in red and yellow-highlights) for the complexes.	S16
Reference	S16

Materials: All the chemicals and solvents were obtained from commercial sources and were used as supplied, unless noted otherwise. 3,5-di-*tert*-butylcatechol, 2-fluoronitrobenzene, 10% Pd/C, Co(ClO₄)₂•6H₂O, and NaH were purchased from Sigma-Aldrich. Solvents were obtained from Merck (India).

Physical Methods: X-ray crystallographic data were collected using a SuperNova, (Single source at offset, Eos) diffractometer, equipped with a sealed tube Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. Structure was solved with the Superflip, structure solution program using Charge Flipping and refined by direct methods using SHELXS-97 and with full-matrix least squares on F^2 using SHELXL-97.¹ All the non-hydrogen atoms were refined anisotropically. IR spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). UV-Vis spectra were recorded on Perkin Elmer, Lambda 750, UV/VIS/NIR spectrometer preparing a known concentration of the samples in HPLC Grade CH₂Cl₂ at room temperature using cuvette of 1 cm width. EPR spectra were measured on X-Band Microwave Unit, JES-FA200 ESR spectrometer. Magnetic measurement was performed using SQUID magnetometer at 1T external magnetic field. ESI-MS measurement were performed using either Q-TOF LC/MS mass spectrometer (6520, Agilent Technologies) or using quadrupole time-of-flight (QTOF)-MS spectrometer ('Waters, Model: Q-Tof Premier') and peaks are given in m/z (% of basis peak). NMR measurements were done using BRUKER (400 or 600 MHz) NMR machine.

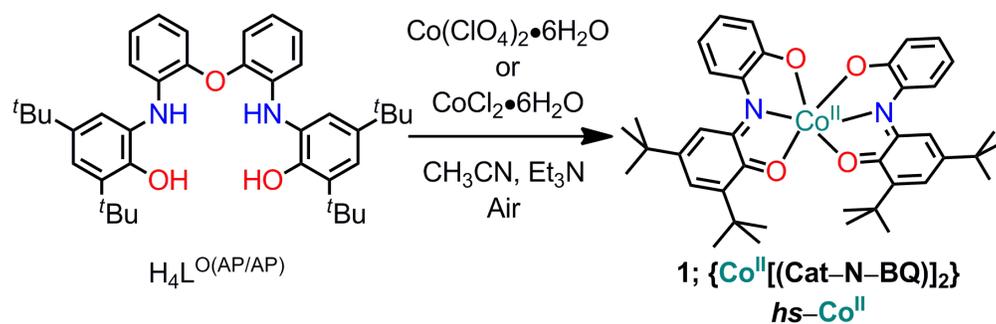


Scheme S1. Synthetic route of $H_4L^{O(AP/AP)}$.

Step1: Synthesis of 2-(2-nitrophenoxy)aniline; (I). To a solution of 2-fluoronitrobenzene (0.987 g, 7 mmol) in dry DMF (4 mL), *o*-aminophenol (0.763 g, 7 mmol) and sodium hydride (0.336 g, 14 mmol) were added sequentially under Ar-atmosphere at ice cold condition. The reaction mixture was turned to reddish in due course. After 15 min, the reaction mixture was allowed to stir at room temperature for 18 h. Then it was quenched with water under ice cold condition and the product was extracted with CH_2Cl_2 (3×40 mL). The combined organic portion was then washed with water and brine solution and dried over anhydrous Na_2SO_4 . Solvent was removed and the residue was dried under high vacuum. Thus obtained oily residue was purified by column chromatography on silica gel with an eluent consisting of hexane/ethyl acetate (9:1). 2-(2-nitrophenoxy)aniline was appeared as orange liquid. Yield: 1.432 g, 89%. FTIR (KBr pellet, cm^{-1}): 3462, 3384, 1624, 1605, 1586, 1525, 1500, 1352, 1307, 1270, 1238, 1186, 889, 777, 742, 665. 1H NMR ($CDCl_3$, 399.853 MHz): δ 7.91 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 7.47–7.43 (m, 1H), 7.15–7.11 (m, 1H), 7.08–7.04 (m, 1H), 6.96–6.93 (m, 2H), 6.86–6.84 (m, 1H), 6.77–6.73 (m, 1H), 3.95 (s, 2H) ppm. ESI-MS (+) m/z for $[C_{12}H_{10}N_2O_3 + H]^+$: Calcd, 231.08; found, 231.08.

Step2: Synthesis of bis(*o*-aminophenyl) ether; (II). To a methanolic solution (15 mL) of 2-(2-nitrophenoxy)aniline (1.217 g, 5.29 mmol), 10% Pd in charcoal (35 mg) was added under argon atmosphere at ice cold condition. After a while (5 min), ammoniumformate (3.066 g, 48.6 mmol) was added to the reaction solution. The reaction mixture was then allowed to stir at room temperature for 4 h under argon atmosphere. It was then filtered through a pad of celite. The pad was washed with CH₂Cl₂ (50 mL). The filtrate was then extracted with CH₂Cl₂ (3×40 mL). The combined organic portion was washed with water and brine solution and dried over anhydrous Na₂SO₄. After evaporating the solvent, an off-white solid was obtained as the product. Yield: 0.941 g, 89%. FTIR (KBr pellet, cm⁻¹): 3469, 3426, 3379, 3348, 3200, 3061, 3034, 1615, 1580, 1499, 1454, 1303, 1263, 1199, 1185, 1156, 1137, 1033, 886, 794, 754, 678. ¹H NMR (399.850 MHz, CDCl₃): δ 6.98–6.94 (m, 2H), 6.83–6.80 (m, 2H), 6.72–6.69 (m, 2H), 3.89 (s, 4H) ppm. ¹³C NMR (100.55 MHz, CDCl₃): δ 143.9, 138.0, 124.3, 118.8, 118.3, 116.4 ppm. ESI-MS (+) for [C₁₂H₁₂N₂O + H]⁺: Calcd, 201.10; found, 201.10.

Step3: Synthesis of H₄L^{O(AP/AP)}. To a suspension of bis(*o*-aminophenyl) ether (0.891 g, 4.45 mmol) in hexane (15 mL), 3,5-di-*tert*-butylcatechol (1.979 g, 8.90 mmol) and Et₃N (0.05 mL) were added sequentially and the reaction mixture was refluxed for 30 min. After that the solution was stirred at room temperature (30 °C) for another 24 h. The solvent was evaporated and dried. The residue was dissolved in hot methanol. A white precipitate was separated out from the methanolic solution. The solid was filtered and washed with methanol (10 mL) and dried. Yield: 1.731 g, 64 %. FTIR (KBr pellet, cm⁻¹): 3437, 3377, 3056, 2958, 2906, 2868, 1609, 1599, 1587, 1504, 1483, 1460, 1448, 1425, 1391, 1363, 1316, 1241, 1224, 1195, 1156, 1117, 1106, 1040, 975, 879, 824, 767, 742, 579. ¹H NMR (399.893 MHz, CDCl₃): δ 7.23 (d, *J* = 2.0 Hz, 2H), 7.04 (d, *J* = 2.0 Hz, 2H), 7.00–6.94 (m, 4H), 6.84–6.80 (m, 2H), 6.63–6.60 (m, 2H), 6.34 (s, 2H), 5.58 (s, 2H), 1.44 (s, 18H), 1.26 (s, 18H) ppm. ¹³C NMR (150.93 MHz, CDCl₃): δ 149.7, 144.5, 142.5, 138.4, 135.7, 127.4, 124.8, 122.3, 121.7, 120.0, 117.9, 115.5, 35.2, 34.6, 31.8, 29.8 ppm. ESI-MS (+) *m/z* for [C₄₀H₅₂N₂O₃ + H]⁺: Calcd, 609.40; found, 609.41.



Scheme S2. Synthetic route of complex **1**; {Co^{II}[(Cat-N-BQ)]₂}.

Synthesis of complex C₄₀H₄₈CoN₂O₄; 1. Co(ClO₄)₂·6H₂O (0.366 g, 1.0 mmol) and Et₃N (0.4 mL) were added sequentially to a suspension of H₄L^{O(AP/AP)} (0.608 g, 1.0 mmol) in CH₃CN (20 mL). A brown precipitate was observed initially within 10 min which turned black with time. After stirring for 7 h at room temperature, the resulting precipitate was filtered and washed with acetonitrile. The solid was crystallized from a mixture of chloroform/acetonitrile (3:1) solution by slow evaporation process. Yield: 0.204 g, 57 %; 0.161 g, 45 % (when CoCl₂·6H₂O was used as the metal ion source). FTIR (KBr pellet, cm⁻¹): 3060, 2951, 2906, 2867, 1592, 1523, 1479, 1451, 1400, 1384, 1367, 1322, 1310, 1289, 1261, 1202, 1173, 1145, 1130, 1099, 1022, 978, 903, 796, 741, 585, 532, 497. ESI-MS (+) *m/z* for [C₄₀H₄₈CoN₂O₄]⁺: Calcd, 679.29; found, 679.30. UV-Vis/NIR (CH₂Cl₂, 300 K) λ_{max}, nm (ε, M⁻¹cm⁻¹): 1200 (1200), 1001 (6650), 762 (14400), 688^{sh} (13700), 511 (11300), 428 (14750), 387 (25700). Anal. Calcd for C₄₀H₄₈N₂O₄Co·0.3CHCl₃ [crystallized from chloroform/acetonitrile (3:1) solvent mixture]: C, 67.64; H, 6.80; N, 3.91. Found: C, 67.68; H, 7.00; N, 4.01. Anal. Calcd for C₄₀H₄₈N₂O₄Co·0.8CH₃CN [crystallized from a diethyl ether/acetonitrile (2:1) solvent mixture]: C, 70.12; H, 7.13; N, 5.50. Found: C, 71.71; H, 7.00; N, 5.52. Anal. Calcd for C₄₀H₄₈N₂O₄Co (crystallized from toluene): C, 70.68; H, 7.12; N, 4.12. Found: C, 70.03; H, 6.99; N, 4.23.

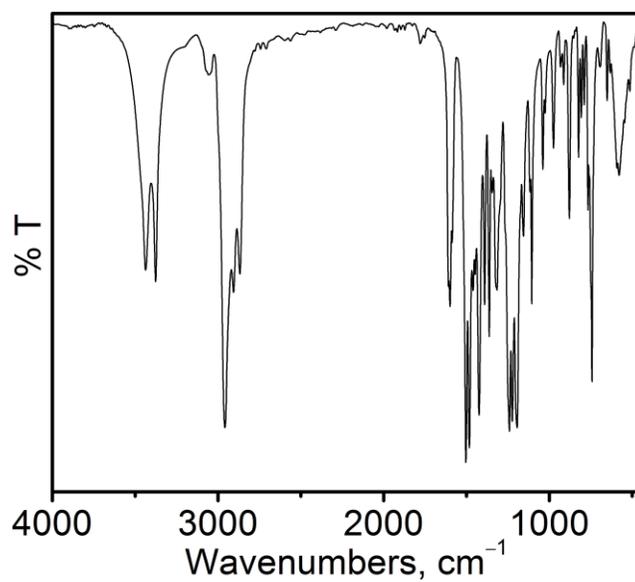


Figure S1: IR spectrum of ligand $H_4L^{O(AP/AP)}$.

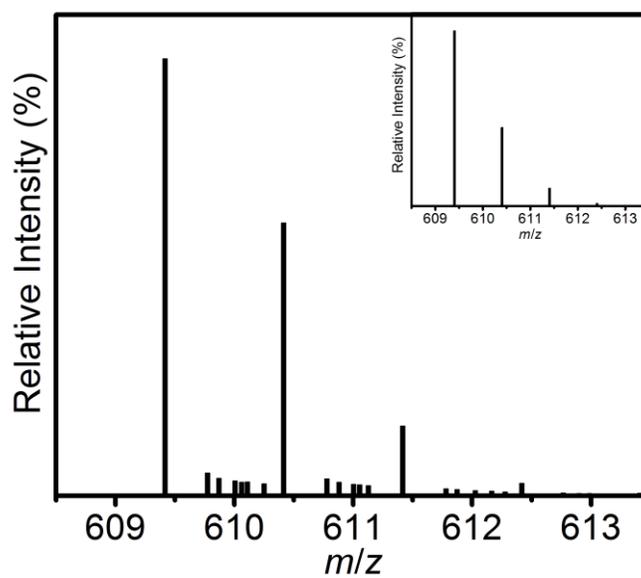


Figure S2: ESI-mass spectrum of ligand $H_4L^{O(AP/AP)}$ in +ve mode corresponded to $[L+H]^+$ molecular ion peak having composition $[C_{40}H_{52}N_2O_3+H]^+$; experimental and calculated isotope distribution pattern (inset). The measurement was done in CH_3CN solution.

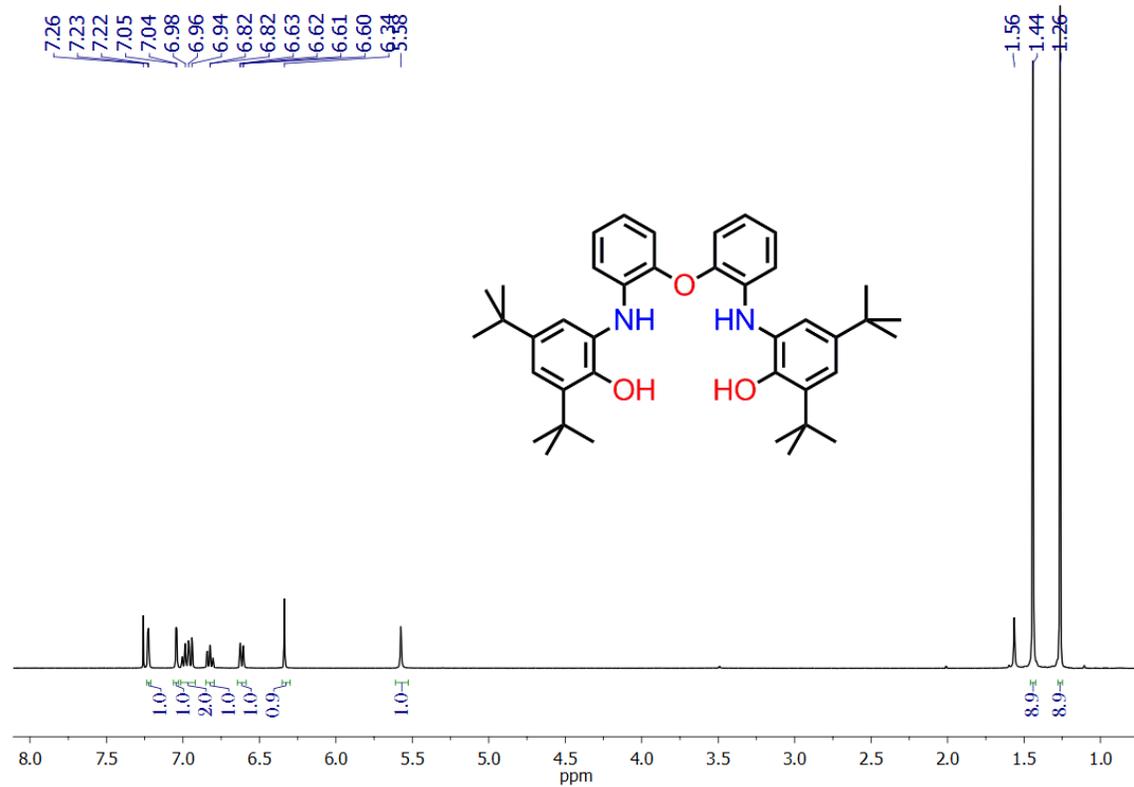


Figure S3: ^1H NMR spectrum of ligand $\text{H}_4\text{L}^{\text{O}(\text{AP}/\text{AP})}$ in CDCl_3 at 399.893 MHz.

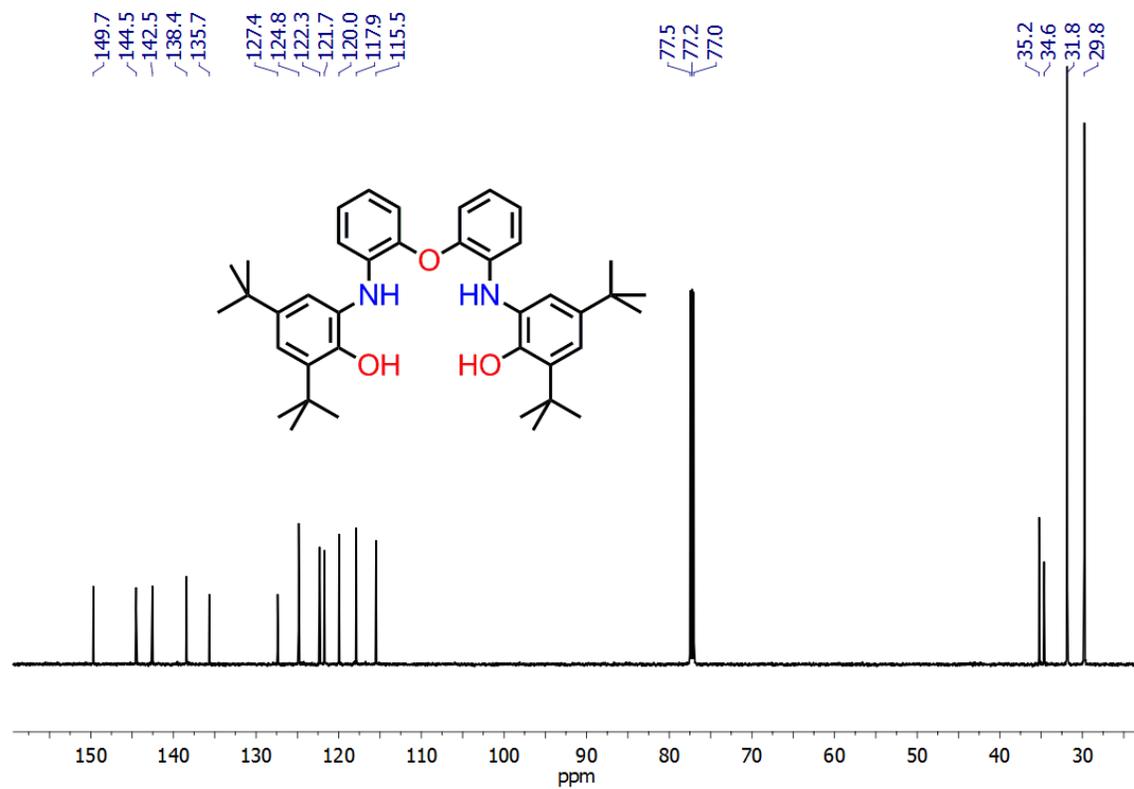


Figure S4: ^{13}C NMR spectrum of ligand $\text{H}_4\text{L}^{\text{O}(\text{AP}/\text{AP})}$ in CDCl_3 at 150.93 MHz.

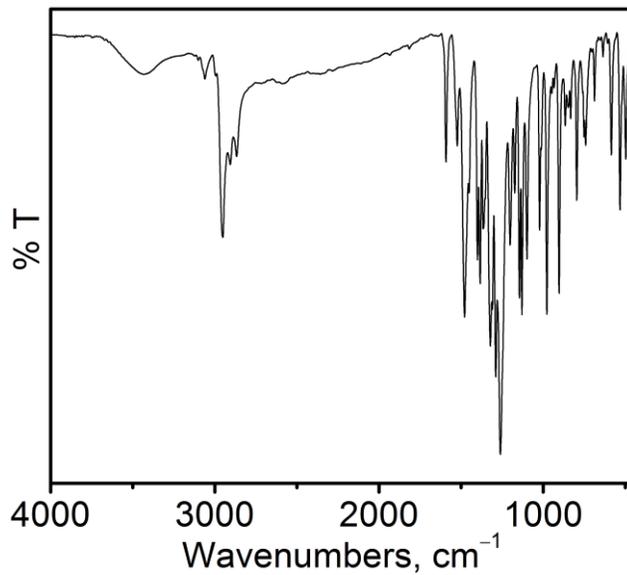


Figure S5: IR Spectrum of complex $1 \cdot 0.3\text{CHCl}_3$.

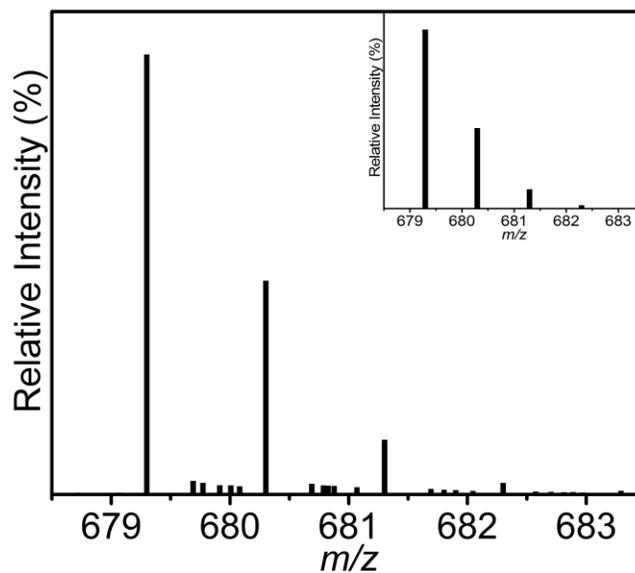
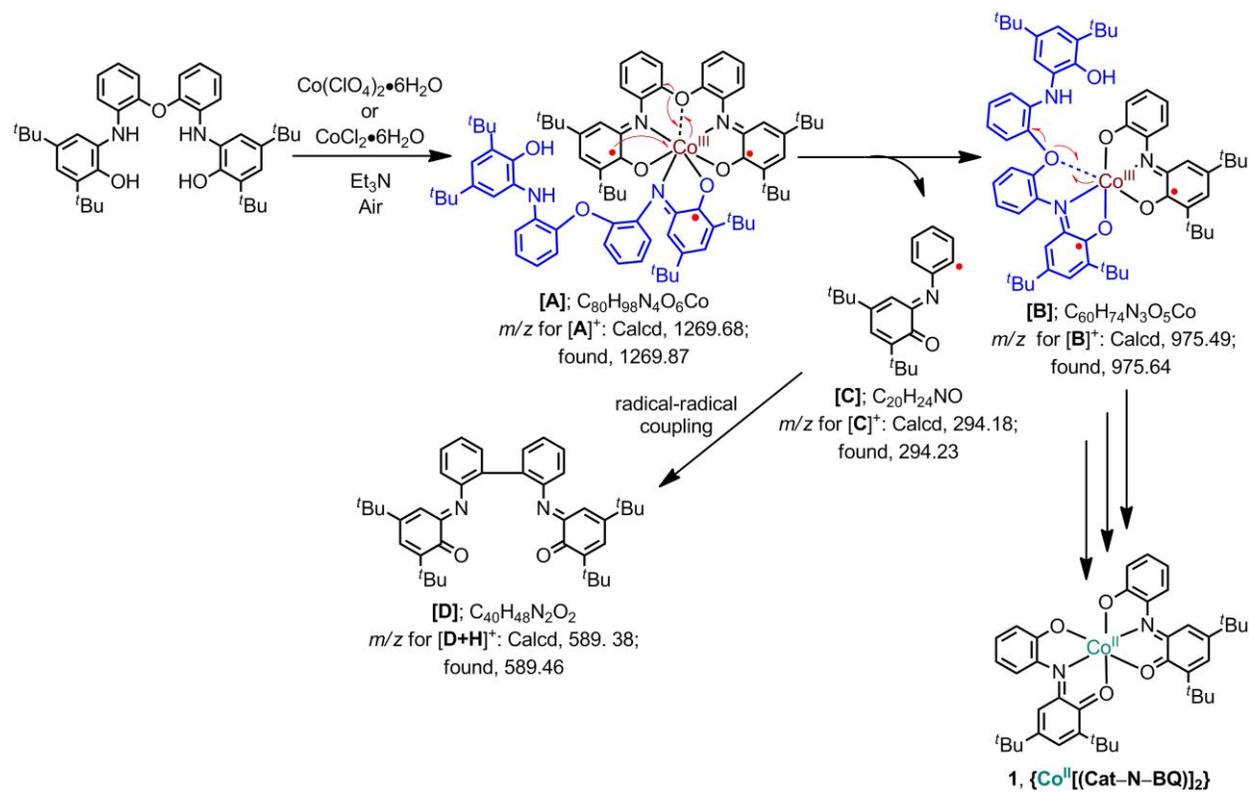


Figure S6: ESI-mass spectrum of complex $1 \cdot 0.3\text{CHCl}_3$ in +ve mode corresponded to $[M]^+$ molecular ion peak having composition $[\text{C}_{40}\text{H}_{48}\text{CoN}_2\text{O}_4]^+$; experimental and calculated isotope distribution pattern (inset). The measurement was done in CH_3CN solution.



Scheme S3: Proposed mechanism of the formation of complex **1** from $\text{H}_4\text{L}^{\text{O}(\text{AP}/\text{AP})}$.

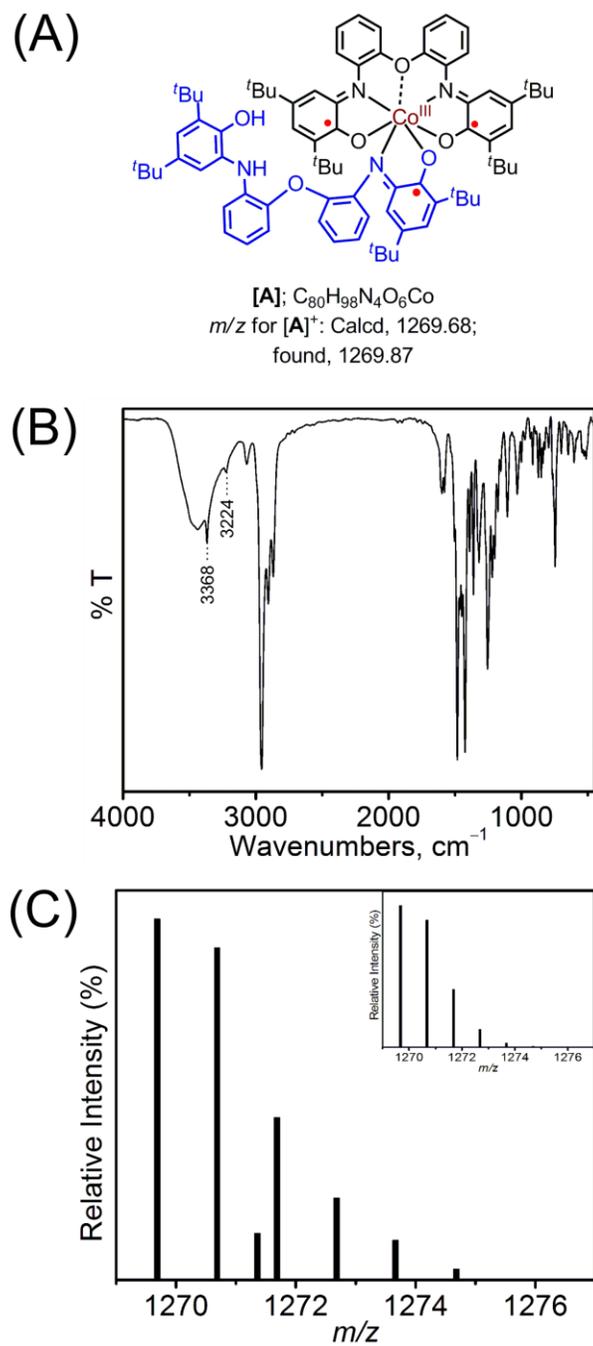


Figure S7: (A) Intermediate A; (B) FTIR (KBr pallet) spectrum of the intermediate and (C) ESI-MS (+) spectrum of the intermediate in CH₃CN.

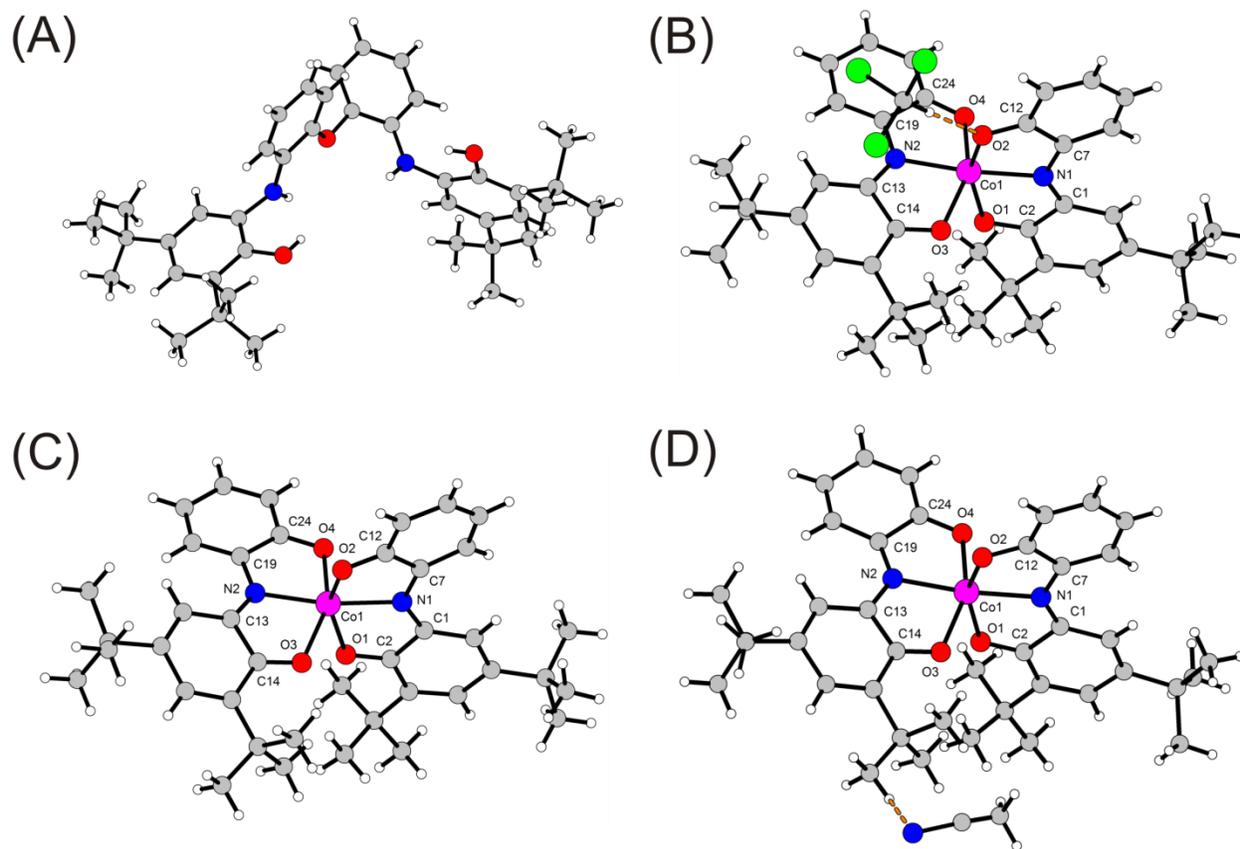


Figure S8: Molecular structure of (A) ligand $H_4L^{O(AP/AP)}$; (B) complex $1 \cdot 1CHCl_3$; $C_{40}H_{48}CoN_2O_4 \cdot CHCl_3$ (crystallized from a 3:1 chloroform and acetonitrile solvent mixture); (C) complex **1**; $C_{40}H_{48}CoN_2O_4$ (crystallized from toluene) and (D) complex $1 \cdot 1CH_3CN$; $C_{40}H_{48}CoN_2O_4 \cdot CH_3CN$ (crystallized from a 2:1 diethyl ether and acetonitrile solvent mixture).

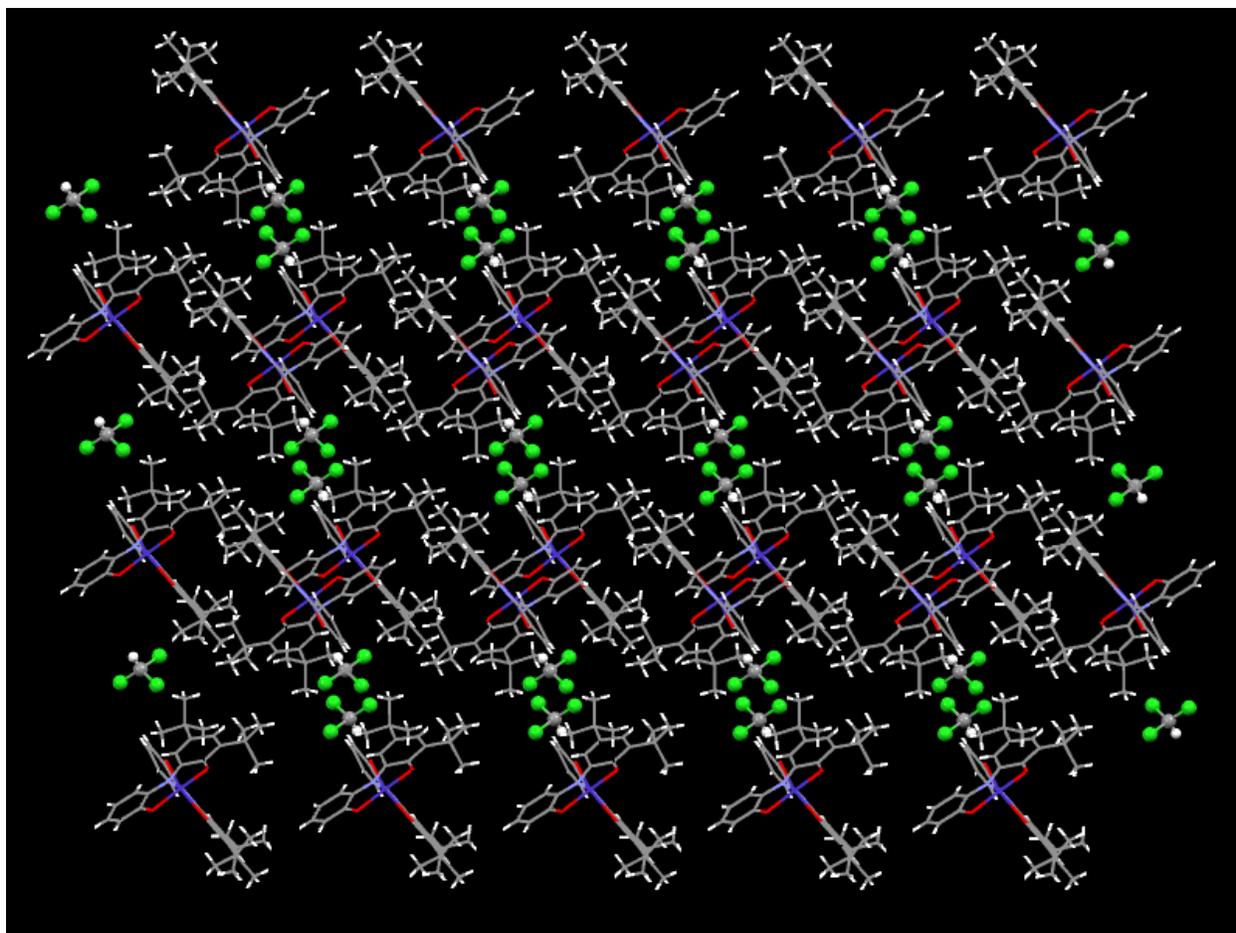


Figure S9: Crystal packing diagram of complex **1**•ICHCl₃ along *c*-axis. The elements C, Co, Cl, H, O and N are represented as gray, blue, green, white, red and violet color, respectively.

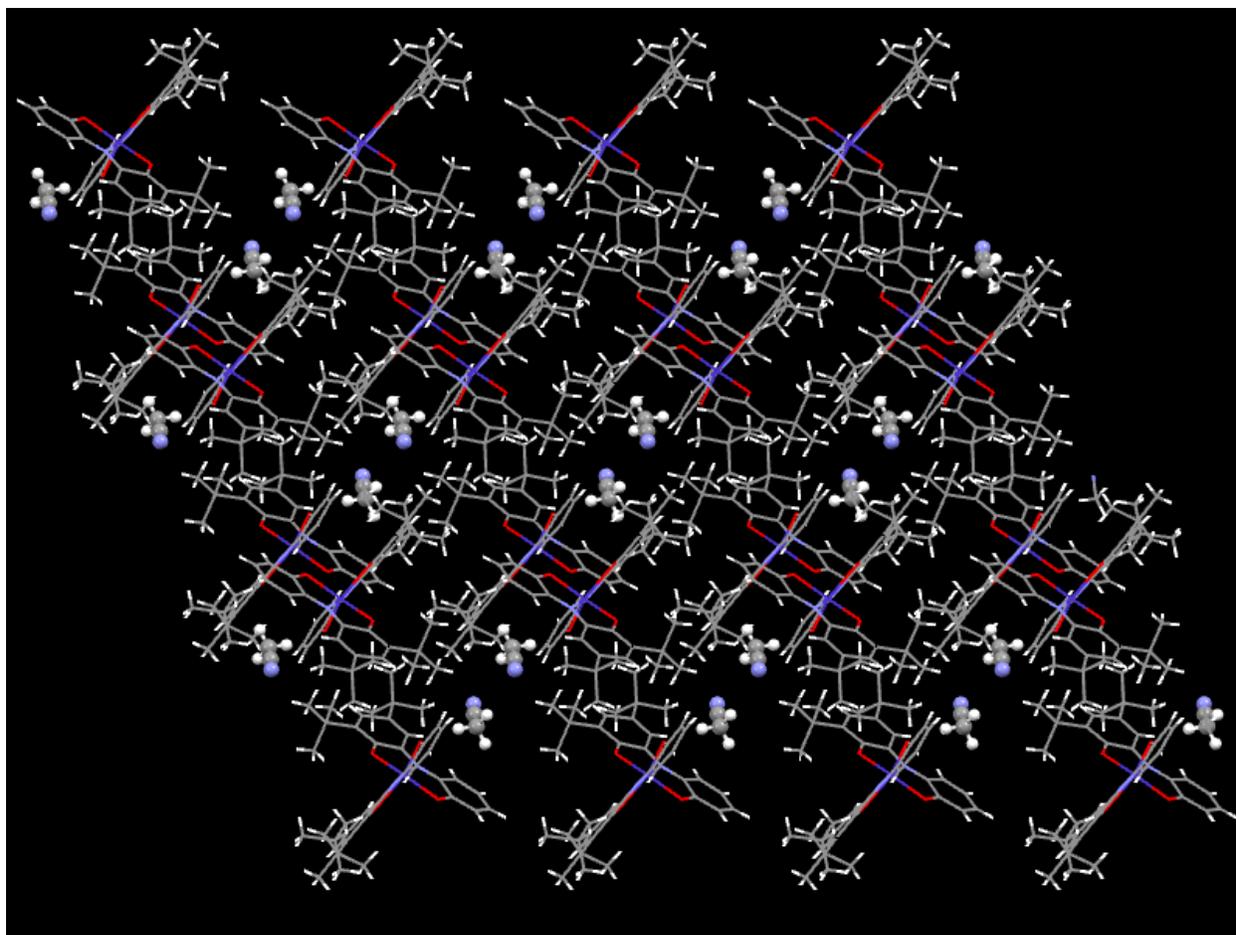


Figure S10: *Crystal packing diagram of complex $1 \bullet \text{ICH}_3\text{CN}$ along c -axis. The elements C, Co, H, O and N are represented as gray, blue, white, red and violet color, respectively.*

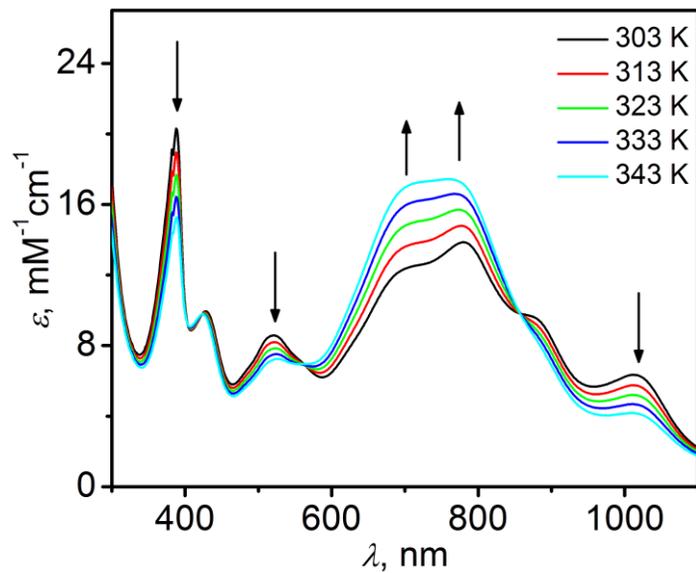


Figure S11: Temperature dependent electronic absorption spectra of complex **1** in toluene over a temperature range 303–343 K.

Table S1. Selected bond distances (Å) for the Co complexes.

Bond	1 •1CHCl ₃ (293 K)	1 (100 K)	1 •1CH ₃ CN (293 K)
Co1–O1	2.113(10)	2.103(5)	2.113(6)
Co1–O2	2.027(12)	2.049(5)	2.049(7)
Co1–O3	2.089(9)	2.107(5)	2.056(9)
Co1–O4	2.017(10)	2.032(6)	2.063(9)
Co1–N1	2.082(11)	2.062(6)	2.082(6)
Co1–N2	2.083(10)	2.064(6)	2.085(7)
O1–C2	1.266(16)	1.267(8)	1.255(10)
O2–C12	1.292(16)	1.299(8)	1.301(10)
O3–C14	1.271(15)	1.257(8)	1.270(10)
O4–C24	1.234(16)	1.295(9)	1.293(11)
N1–C1	1.287(16)	1.348(9)	1.314(10)
N1–C7	1.391(17)	1.345(9)	1.362(11)
N2–C13	1.355(15)	1.317(9)	1.335(12)
N2–C19	1.393(16)	1.377(9)	1.324(13)

Table S2: Crystallographic data and its quality-limitations (in red and yellow-highlights) for the complexes.

	1•1CHCl₃	1	1•1CH₃CN
Empirical formula	C ₄₁ H ₄₉ CoN ₂ O ₄ Cl ₃	C ₄₀ H ₄₈ CoN ₂ O ₄	C ₄₂ H ₅₁ CoN ₃ O ₄
Formula weight	799.10	679.73	720.79
Unit cell dimensions	a = 11.6599(17) Å b = 13.780(3) Å c = 14.5966(9) Å $\alpha = 78.503(10)^\circ$ $\beta = 88.721(8)^\circ$ $\gamma = 81.580(14)^\circ$	a = 10.741(2) Å b = 13.763(3) Å c = 14.309(3) Å $\alpha = 64.820(5)^\circ$ $\beta = 86.451(5)^\circ$ $\gamma = 72.227(6)^\circ$	a = 11.9760(11) Å b = 13.4487(11) Å c = 14.6400(7) Å $\alpha = 67.872(6)^\circ$ $\beta = 88.335(6)^\circ$ $\gamma = 65.421(9)^\circ$
Volume, V (Å ³)	2273.4(5)	1817.2(6)	1963.4(3)
Z	2	2	2
Temperature, T(K)	293(2)	100(2)	293(2)
θ range for data collection	2.95° to 25.00°	1.58° to 18.81°	3.02° to 25.00°
Completeness to θ	99.4% ($\theta = 25.00^\circ$)	97.6% ($\theta = 18.81^\circ$)	95.6% ($\theta = 25.00^\circ$)
Goodness-of-fit on F^2	0.929	1.036	1.172
R(int)	0.1846	0.0689	0.1275
R(sigma)	0.2595	0.0950	0.1469
Final R indices [$I > 2\sigma(I)$]	$RI = 0.1794$, $wR2 = 0.3740$	$RI = 0.0566$, $wR2 = 0.1267$	$RI = 0.1193$, $wR2 = 0.2998$
R indices (all data)	$RI = 0.2901$, $wR2 = 0.4418$	$RI = 0.0986$, $wR2 = 0.1506$	$RI = 0.2027$, $wR2 = 0.4067$

Reference:

1. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.