

Electronic Supporting Information

for the

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Cobalt Complexes as the Building Blocks: {Co³⁺ - Zn²⁺}
Heterobimetallic Networks and their Properties

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Material and Methods. Unless otherwise noted, starting materials were obtained from the commercial sources and used without further purification. Prior to use, solvents were purified following the standard procedures. Ligand H_2L^2 and H_2L^3 were synthesized according to the modified reported procedures.^{1,2}

Synthesis.

Synthesis of $\text{Et}_4\text{N}[\text{Co}(\text{L}^2)_2]$ (2**).** A mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.195g, 0.782 mmol), ligand H_2L^2 (0.50g, 1.565 mmol), and K_2CO_3 (5.41g, 39.14 mmol) were taken in 50 mL of CH_2Cl_2 and the reaction mixture was refluxed for 4 h. To the resultant deep red solution, solid $\text{Et}_4\text{NCl} \cdot x\text{H}_2\text{O}$ (0.311g, 1.879 mmol) was added and the mixture was further stirred in open air for 2 h at room temperature. Exposure to the air resulted in a deep green colored solution. The mixture was filtered and the volatiles were removed under reduced pressure to afford the crude compound. Recrystallization was achieved by dissolving the crude product in CH_3CN and subjecting to the vapor diffusion of diethyl ether. This resulted in a highly crystalline product in a day. Yield: 0.50g (77%). Anal. Calcd. for $\text{C}_{42}\text{H}_{42}\text{CoN}_{11}\text{O}_4 \cdot 2\text{H}_2\text{O}$: C, 58.67; H, 5.39; N, 17.92. Found: C, 58.17; H, 5.45; N, 17.35%. FT-IR spectrum (KBr, ν , selected peaks): 3058, 2986 (CH); 1615, 1594 (C=O) cm^{-1} . Absorption spectrum [λ_{max} , nm, DMSO (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 640 (125). ESI-MS (CH_3CN , m/z): calcd. for $\text{C}_{42}\text{H}_{42}\text{CoN}_{11}\text{O}_4$, 823.2753; found, 823.2813. ^1H NMR spectrum [DMSO- d_6 , 300 MHz, 25°C, TMS]: δ 8.01-8.07 (*m*, 6H, H^1/H^2), 7.87 (*s*, 4H, H^9), 7.67 (*d*, $J = 7.8$ Hz, 4H, H^8), 6.94-7.03 (*m*, 8H, H^6/H^7), 3.15 (*q*, $J = 7.2$ Hz, 8H), 1.11 (*t*, $J = 6.3$ Hz, 12H).

Synthesis of $\text{Et}_4\text{N}[\text{Co}(\text{L}^3)_2]$ (3**).** A similar synthetic procedure was followed as that of complex **2** using following reagents: $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.195g, 0.782 mmol), ligand H_2L^2 (0.50g, 1.565 mmol), K_2CO_3 (5.41g, 39.14 mmol), and $\text{Et}_4\text{NCl} \cdot x\text{H}_2\text{O}$ (0.311g, 1.879 mmol). Yield: 0.45g (70%). Anal. Calcd. for $\text{C}_{42}\text{H}_{42}\text{CoN}_{11}\text{O}_4 \cdot \text{H}_2\text{O}$: C, 59.92; H, 5.27; N, 18.30. Found: C, 59.50; H, 5.45; N, 17.95%. FT-IR spectrum (KBr, ν , selected peaks): 3077, 2984 (CH); 1617, 1582 (C=O) cm^{-1} . Absorption spectrum [λ_{max} , nm, DMSO (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 638 (105). ESI-MS (CH_3CN , m/z): calcd. for $\text{C}_{42}\text{H}_{42}\text{CoN}_{11}\text{O}_4$, 823.2753; found, 823.2734. ^1H NMR spectrum [DMSO- d_6 , 300 MHz, 25°C, TMS]: δ 8.06-8.15 (*m*, 6H, H^1/H^2), 7.76 (*d*, $J = 7.2$ Hz, 8H, H^7/H^8), 6.58 (*d*, $J = 5.7$ Hz, 8H, H^6/H^9), 3.17 (*q*, $J = 7.2$ Hz, 8H), 1.14 (*t*, $J = 6.0$ Hz, 12H).

Synthesis of network $\{[(\mathbf{2})\text{-Zn}(\text{OH})_2\text{DMF}]\text{NO}_3\}_n$ (2a**).** Heterobimetallic network **2a** was synthesized by layering a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.073g, 0.243 mmol) in 4 mL CH_3OH over a solution of complex **2** (0.10g, 0.121 mmol) in 2:1 (v/v) mixture of DMF and CH_3OH (5 mL).

After a period of three to four days, brown colored highly crystalline product was obtained which was also suitable for the crystallographic studies. The product was isolated and dried under vacuum. Yield: 0.084g (65%). Anal. Calcd. for $C_{40}H_{34}CoN_{14}O_{14}Zn$: C, 45.36; H, 3.34; N, 18.52. Found: C, 45.96; H, 3.74; N, 18.47%. FT-IR spectrum (KBr, ν , selected peaks): 3424 (OH); 1591(C=O) and 1385 (NO_3^-) cm^{-1} . Absorption spectrum [λ_{max} , nm, DMSO (ϵ , $M^{-1} cm^{-1}$)]: 646 (240).

Synthesis of network $\{[(3)_6-Zn_5(OH_2)_7](NO_3)_4\}_n$ (3a). Heterobimetallic network **3a** was synthesized by layering a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.073g, 0.243 mmol) in 2 mL H_2O over a solution of **3** (0.10g, 0.121 mmol) in 2:1 (v/v) mixture of DMF and H_2O (5 mL). After a period of one week, green colored highly crystalline product was obtained which was also suitable for the crystallographic studies. The product was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.069g (63%). Anal. Calcd. for $C_{204}H_{132}Co_6N_{66}O_{74}Zn_5$: C, 45.96; H, 3.74; N, 17.47. Found: C, 45.61; H, 3.48; N, 17.21%. FT-IR spectrum (KBr, ν , selected peaks): 3422 (OH); 1628, 1591 (C=O) and 1385 (NO_3^-) cm^{-1} . Absorption spectrum [λ_{max} , nm, DMSO (ϵ , $M^{-1} cm^{-1}$)]: 645 (240).

Physical Methods. The FT-IR spectra (KBr disk, 4000-400 cm^{-1}) were recorded on a Perkin-Elmer FTIR 2000 spectrometer. Adsorption spectra were recorded using Perkin-Elmer *Lambda*-25 spectrophotometer. ESI-MS mass spectra were obtained from the LC-TOF (KC-455) mass spectrometer of Waters. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies were performed on DTG – 60 SHIMADZU and TA DSC Q 200 instruments, respectively, at 5 $^{\circ}C/min$ heating rate under the nitrogen atmosphere. 1H NMR and ^{13}C NMR spectra were recorded on Avance Bruker instrument (300 MHz) in DMSO with TMS as the internal standard. Microanalysis data were obtained from the Elementar Analysen Systeme GmbH Vario EL-III instrument. Adsorption isotherms were measured in an AUTOSORB-1C, Quantachrome, USA instrument. Under the continuous adsorption conditions, prior to measurement, samples were heated at 350 $^{\circ}C$ for 12 h where Helium gas used for the flushing propose. The N_2 adsorption measurements were performed at 77 K and 298 K. The X – ray powder diffraction studies was performed on a Bruker AXS, model – D8 Discover ($CuK\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$). The samples were grinded and subjected to the range of $2\theta - 30\theta$ with the step angle of 0.01° and step time of 0.1s at room temperature.

Single Crystal X-ray Structural Studies. The single crystal X-ray diffraction data were collected either on an Oxford XCalibur³ CCD (for complexes **2** and **3**) or a Bruker Kappa Apex^{4,5} CCD (for complex **2a** and **3a**) diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The intensity data were corrected for Lorentz polarization effects, and an empirical absorption correction (SADABS) was applied.⁶ The structures were solved by the direct methods and refined by the full-matrix least-squares refinement techniques on F^2 using the program SHELXL-97 in WinGX module.⁷ All hydrogen atoms were fixed at the calculated positions with isotropic thermal parameters and all non hydrogen atoms were refined anisotropically. The hydrogen atoms of the coordinated water molecule were located from the difference Fourier synthesis whereas the hydrogen atoms of the uncoordinated water molecules could not be found in the difference Fourier map for complex **3a**. All other hydrogen atoms were placed in the calculated positions using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. The asymmetric unit cell of complex **2** consisted of two independent molecules along with two tetraethyl ammonium cations and a water molecule. In contrast, the unit cell of complex **3** consisted of half molecule and symmetry transformations were used to generate the equivalent atoms. The crystal structure of complex **3** had disorder and/or partial occupancy complications with the tetraethylammonium cation (N11, C35, C36, C37 and C38 atoms) which were resolved using DFIX command and the atoms were further refined anisotropically. The crystal structure of network **3a** also had disorders in some of the uncoordinated water molecules and a nitrate ion. Due to this disorder, these atoms had relatively higher thermal parameters. Further, the highly disordered uncoordinated water molecules O5W, O6W, O7W, and O8W were removed by the 'SQUEEZE' routine of the PLATON program⁸ successfully and the remaining structure was then refined again with the new solvent free reflection data to give a converged improved model. As a result of the solvent removal, the final structure shows solvent accessible voids of volume 564 \AA^3 ($Z = 3$) which correspond to 4.5 water molecules. Output of the Platon SQUEEZE routine has been appended to the CIF file. However, the disorder in the nitrate ion could not be resolved. Details of the crystallographic data and structural refinement parameters are given in Table S1.

General procedure for the Cyanosilylation Reaction. 2 mol% catalyst was taken in a dry round bottom flask and suspended in CH_3CN (5 mL) under the N_2 atmosphere. The respective imine (1.0 equiv) was gradually added to the reaction mixture at room temperature and stirred for

15 min, followed by the drop wise addition of $(\text{CH}_3)_3\text{SiCN}$ (1.0 equiv). The reaction mixture was further stirred for 4h at room temperature. The progress of the reaction was monitored by TLC (10% EtOAc/hexanes). After complete consumption of the imine (~4h), the reaction mixture was filtered to remove the catalyst. The catalyst was washed twice with diethyl ether and dried under vacuum and can be reused without further purification or regeneration. The filtrate was evaporated under reduced pressure and the residue was dissolved in CH_3OH and quenched with 1N HCl. The solvent was removed and the residue was washed with water. The residue was again dissolved in CH_2Cl_2 and dried over anhydrous Na_2SO_4 . The filtrate was evaporated to provide the crude product, which was purified by the gradient column chromatography using 60-120 mesh silica and EtOAc/hexane as the eluent.

References:

- (1) S. L. Jain, P. Bhattacharyya, H. L. Milton, A. M. Z. Slawin, J. A. Crayston, J. D. Woollins, *Dalton Trans.* 2004, 862.
- (2) A. Mishra, N. K. Kaushik, A. K. Verma, R. Gupta, *Eur. J. Med. Chem.*, 2008, **43**, 2189.
- (3) CrysAlisPro, Oxford Diffraction Ltd., version 1.171.33.49b, 2009.
- (4) SMART: Bruker Molecular Analysis Research Tool, version 5.618, Bruker Analytical X-ray System, 2000.
- (5) SAINT-NT, Version 6.04, Bruker Analytical X-ray System, 2001.
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- (7) L. J. Farrugia, WinGX version 1.64, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-ray Diffraction Data; Department of Chemistry, University of Glasgow, 2003.
- (8) A.L. Spek, PLATON/SQUEEZE – *A Multi Purpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2002.

Table S1. Summary of X-ray crystallographic data collection and refinement parameters for **2**, **3**, **2a**, and **3a**

	2	3	2a	3a
Emp. Formula	C ₈₄ H ₈₆ Co ₂ N ₂₂ O ₉	C ₄₂ H ₄₂ CoN ₁₁ O ₄	C ₄₀ H ₄₀ CoN ₁₄ O ₁₄ Zn	C ₂₀₄ H ₁₄₄ Co ₆ N ₆₆ O ₅₆ Zn ₅
Formula weight	1665.61	823.80	1065.16	5096.28
Temperature (K)	293(2)	293(2)	100(2)	293(2)
Crystal System	Triclinic	Monoclinic	Triclinic	Trigonal
Space Group	P-1	C 2/c	P-1	R-3
a [Å]	10.2583(7)	17.101(5)	13.241(5)	38.9152(14)
b [Å]	13.8731(16)	10.454(5)	13.802(5)	38.9152(14)
c [Å]	28.5219(16)	23.321(5)	14.081(5)	14.4944(7)
α [°]	89.676(4)	90.000	116.834(5)	90.000
β [°]	81.893(5)	90.893(5)	93.137(5)	90.000
γ [°]	80.586(5)	90.000	90.943(5)	120.00
V [Å ³]	3963.8(4)	4169.0(3)	2290.3(14)	19009.4(13)
Z, Dcalcd [g cm ⁻³]	2, 1.396	4, 1.313	2, 1.545	3, 1.336
Abs.coefficient [mm ⁻¹]	0.493	0.467	0.968	0.930
F [000]	1740	1720	1094	7770
R(int.)	0.0367	0.0222	0.0481	0.1181
Final R indices [I>2sigma(I)]	R1 = 0.0621 wR2 = 0.1443	R1 = 0.0842 wR2 = 0.2308	R1 = 0.0488 wR2 = 0.1175	R1 = 0.0957 wR2 = 0.2756
R indices (all data)	R1 = 0.1081 wR2 = 0.1604	R1 = 0.0918 wR2 = 0.2383	R1 = 0.0763 wR2 = 0.1275	R1 = 0.1614 wR2 = 0.3291
GOF on F ²	1.015	1.046	1.024	1.138
CCDC No.	767586	767587	767585	767588

$$^a R_I = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [wF_o^4]} \right\}^{1/2}$$

Table S2. Selected bond lengths [Å] and angles [°] for the building block complexes **2** and **3**

Complexes	2	3
Co-N1	1.954(2)	1.996(3)
Co-N2	1.954(2)	1.974(3)
Co-N3	1.980(2)	1.996(3)#1
Co-N4	1.956(2)	1.974(3)#1
Co-N5	1.860(2)	1.893(3)
Co-N6	1.858(2)	1.893(3)#1
N1-Co-N2	163.01(9)	161.27(14)
N3-Co-N4	162.51(9)	161.27(14)#1
N5-Co-N6	177.15(10)	175.80(2)#1
N1-Co-N4	90.26(10)	88.70(2)#1
N2-Co-N3	90.42(10)	93.53(15)#1
N1-Co-N5	81.43(10)	80.54(14)
N1-Co-N6	98.32(10)	102.54(14)#1

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

Table S3. Selected bond lengths [Å] for heterobimetallic networks **2a** and **3a**

	2a	3a
Co-N1	1.962(2)	1.984(5)
Co-N2	1.980(2)	1.971(5)
Co-N3	1.967(2) #3	1.949(4)
Co-N4	1.964(2) #2	1.957(5)
Co-N5	1.868(2)	1.862(5)
Co-N6	1.858(2)	1.851(5)
Zn-N7	2.154(2)	2.205(5)
Zn-N8	2.178(2)	2.190(5)
Zn-N9	2.155(2)	-----
Zn-N10	2.163(2)	-----
Zn-O1W	2.143(2)	2.107(4)
Zn-O _(DMF)	2.105(2)	-----
Zn _(TMP) -N9	-----	2.047(8)

Symmetry transformations used to generate equivalent atoms: #2 -x+1,-y+1,-z+1 #3 -x,-y+1,-z+1

Table S4. Selected bond angles [$^{\circ}$] for heterobimetallic networks **2a** and **3a** (geometry around the Co^{3+} center)

	2a	3a
N1-Co-N2	162.79(9)#1	162.80(2)
N1-Co-N3	91.97(9)#3	94.30(2)
N1-Co-N4	90.63(9)#2	88.30(2)
N1-Co-N5	81.47(9)#1	81.70(2)
N1-Co-N6	98.38(9)#1	99.80(2)
N2-Co-N3	90.49(9)#3	87.30(2)
N2-Co-N4	91.93(9)#2	95.10(2)
N2-Co-N5	81.32(9)	81.20(2)
N2-Co-N6	98.83(9)#3	97.40(2)
N3-Co-N4	163.17(9)	162.81(19)
N3-Co-N5	98.25(9)#3	97.37(19)
N3-Co-N6	81.93(9)#3	81.80(2)
N4-Co-N5	98.58(9)#2	99.80(2)
N4-Co-N6	81.23(9)#2	81.00(2)
N5-Co-N6	179.76(9)	178.40(2)

Symmetry transformations used to generate equivalent atoms: #1 $x,y-1,z$ #2 $-x+1,-y+1,-z+1$
#3 $-x,-y+1,-z+1$ #4 $x,y+1,z$

Table S5. Selected bond angles [$^{\circ}$] for heterobimetallic networks **2a** and **3a** (geometry around the Zn^{2+} center)

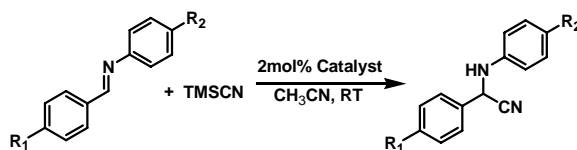
	2a		3a
N7-Zn-N8	90.52(8)	N7-Zn1-N7*	179.996(1)
N7-Zn-N9	173.85(8)	N8*-Zn1-N7	88.86(16)
N7-Zn-N10	91.07(8)	N8*-Zn1-N7*	91.14(16)
N8-Zn-N9	89.76(8)	N8-Zn1-N7*	88.86(16)
N8-Zn-N10	173.02(8)	N8-Zn1-N7	91.14(16)
N9-Zn-N10	89.40(8)	N8*-Zn1-N8	179.998(1)
O1W-Zn-N7	86.63(8)	O1W-Zn1-N7	88.90(18)
O1W-Zn-N8	93.07(8)	O1W*-Zn1-N7	91.10(18)
O1W-Zn-N9	87.22(8)	O1W-Zn1-N7*	91.10(18)
O1W-Zn-N10	93.81(8)	O1W*-Zn1-N7*	88.90(18)
O1S-Zn-N7	94.78(8)	O1W-Zn1-N8	91.94(16)
O1S-Zn-N8	86.29(8)	O1W*-Zn1-N8	88.05(16)
O1S-Zn-N9	91.37(8)	O1W-Zn1-N8*	88.06(16)
O1S-Zn-N10	86.81(8)	O1W*-Zn1-N8*	91.95(16)
O1S-Zn-O1W	178.45(7)	O1W-Zn1-O1W*	179.995(1)

*Symmetry transformations used to generate equivalent atoms: $-x+2/3,-y+1/3,-z+4/3$

Table S6. Gas adsorption and desorption result performed at 77 K and 298 K

Result	2a at 77 K	2a at 298 K	3a at 77 K	3a at 298 K
BET surface area (m ² /g)	5.862	5.337	22.14	17.76
Langmuir surface area (m ² /g)	6.179	5.400	29.63	16.88
Total pore volume (cm ³ /g)	0.013	0.014	0.024	0.45
BJH cumulative desorption surface area (m ² /g)	4.968	16.08	24.72	33.16
BJH cumulative desorption pore volume (m ³ /g)	0.013	0.018	0.025	0.055
BJH desorption pore diameter (Å)	40.46	11.06	34.18	28.88
Average pore diameter (Å)	87.09	10.71	44.44	10.16
Quantity of N ₂ adsorbed (cm ³ /g)	8.3	9.13	15.9	29.16

Table S7. Cyanosilylation reaction of imine with TMSCN using catalysts **2a** and **3a**



S. No. ^[a]	R1	R2	Catalyst 2a %Yield (TON)	Catalyst 3a %Yield (TON)
1	H	H	84 (42)	92 (46)
2 ^[b]	H	H	--- ^[c]	70 (70)
3	F	H	90 (45)	98 (49)
4	Cl	H	90 (45)	96 (48)
5	OMe	H	80 (40)	90 (45)
6	H	F	88 (44)	94 (47)
7	H	Cl	88 (44)	96 (48)
8	H	OMe	90 (45)	96 (48)
9 ^[b]	F	F	--- ^[c]	90 (90)
10 ^[b]	Cl	Cl	--- ^[c]	80 (80)

[a] Catalyst loading: 2mol%; Solvent: CH₃CN; Time: 4h; Temperature: 25°C. [b] Catalyst loading: 1mol%. [c] Not determined.

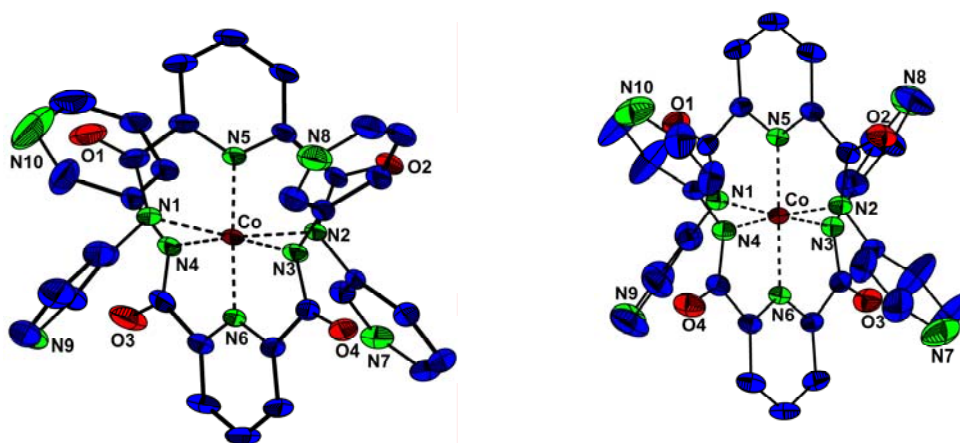


Figure S1. The molecular structures of complex **2** (left) and **3** (right) with partial numbering scheme. Thermal ellipsoids are drawn at 50% probability level. The cation (Et₄N⁺), hydrogen atoms, and water molecule (in case of **2** only) have been omitted for clarity.

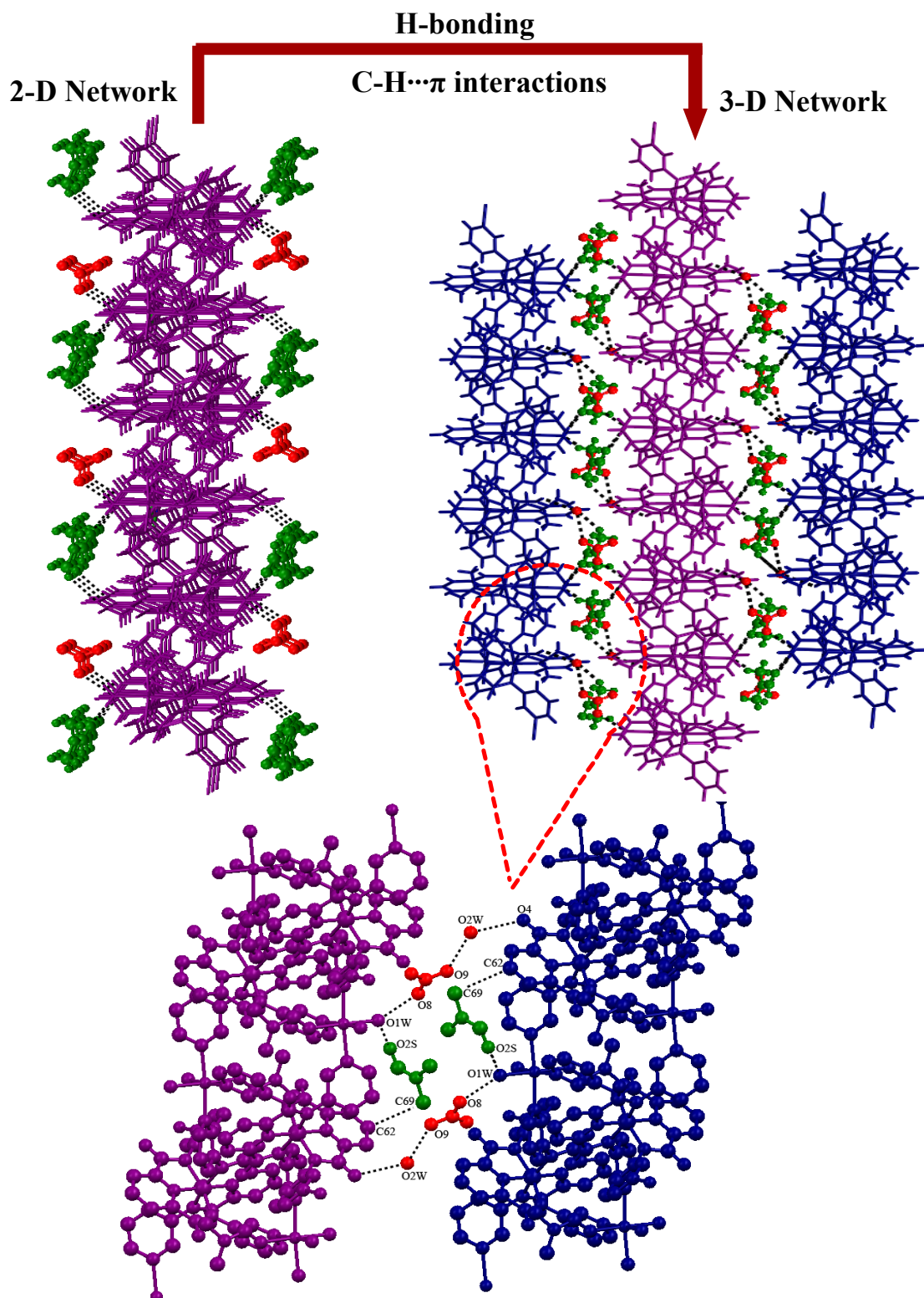


Figure S2. Packing diagram of complex **2a**. See text for details.

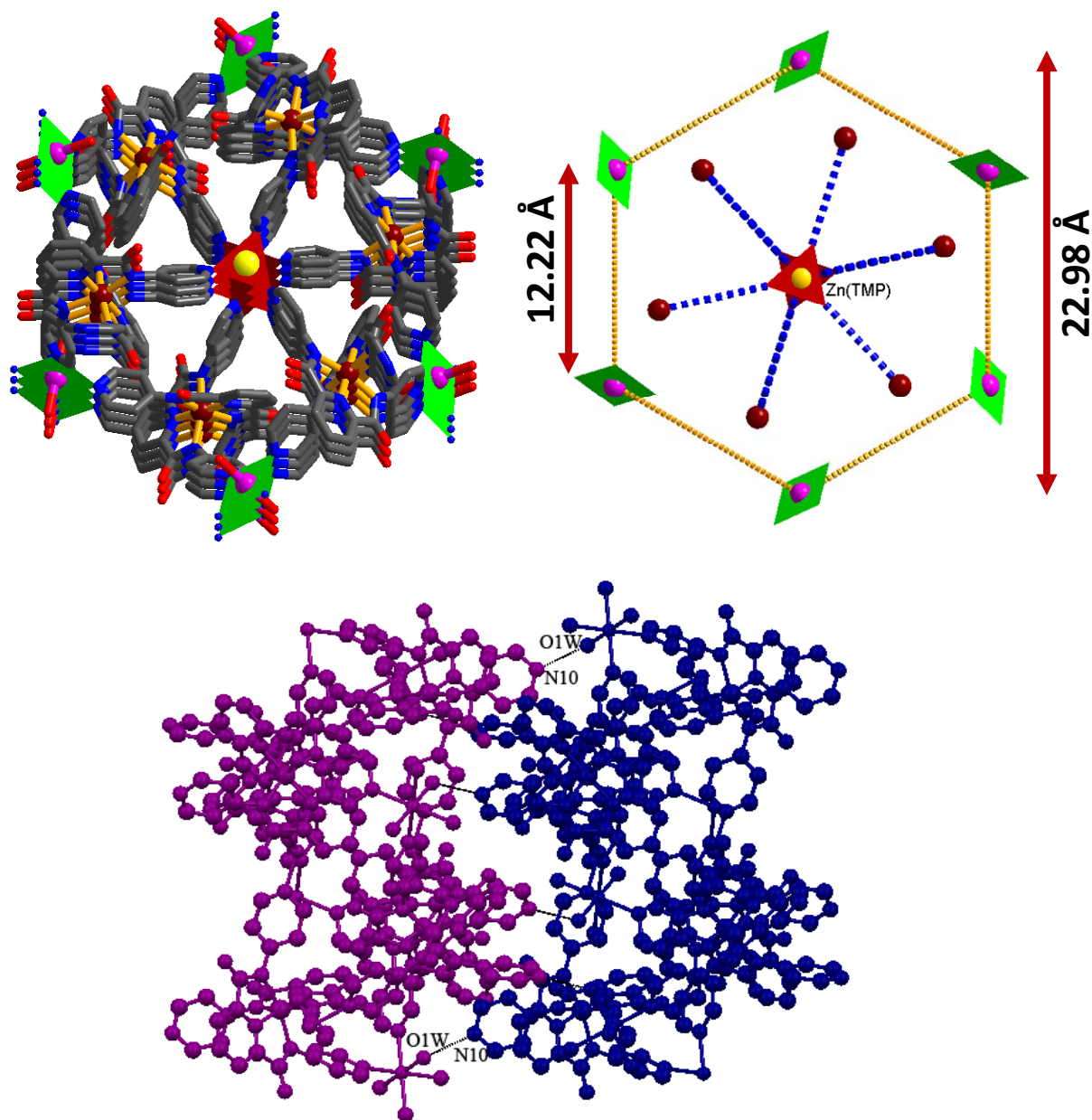


Figure S3. Packing diagram of complex **3a**. View along the crystallographic *c*-axis (upper left); orientation of Co^{3+} and Zn^{2+} ions (upper right). The hydrogen bonding between the uncoordinated pyridine nitrogen atom N10 and water molecule O1W from the neighboring chain, view along the crystallographic *c*-axis (lower).

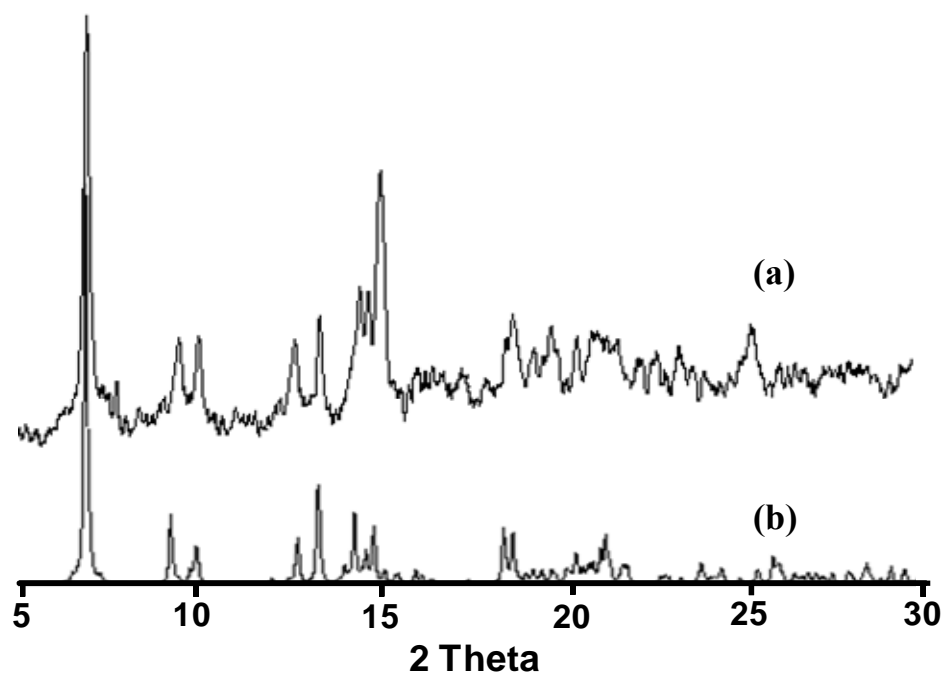


Figure S4. XRPD pattern for network **2a**, bulk sample (a) and the one simulated from the single crystal structure analysis (b) using Mercury 2.3.

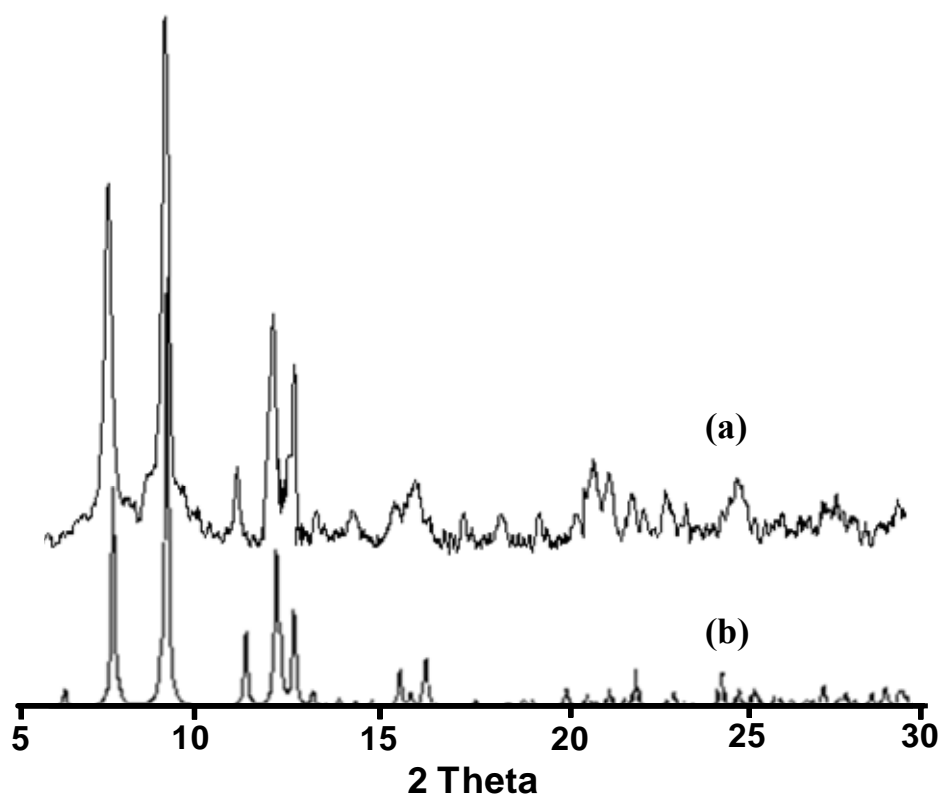


Figure S5. XRPD pattern for network **3a**, bulk sample (a) and the one simulated from the single crystal structure analysis (b) using Mercury 2.3.

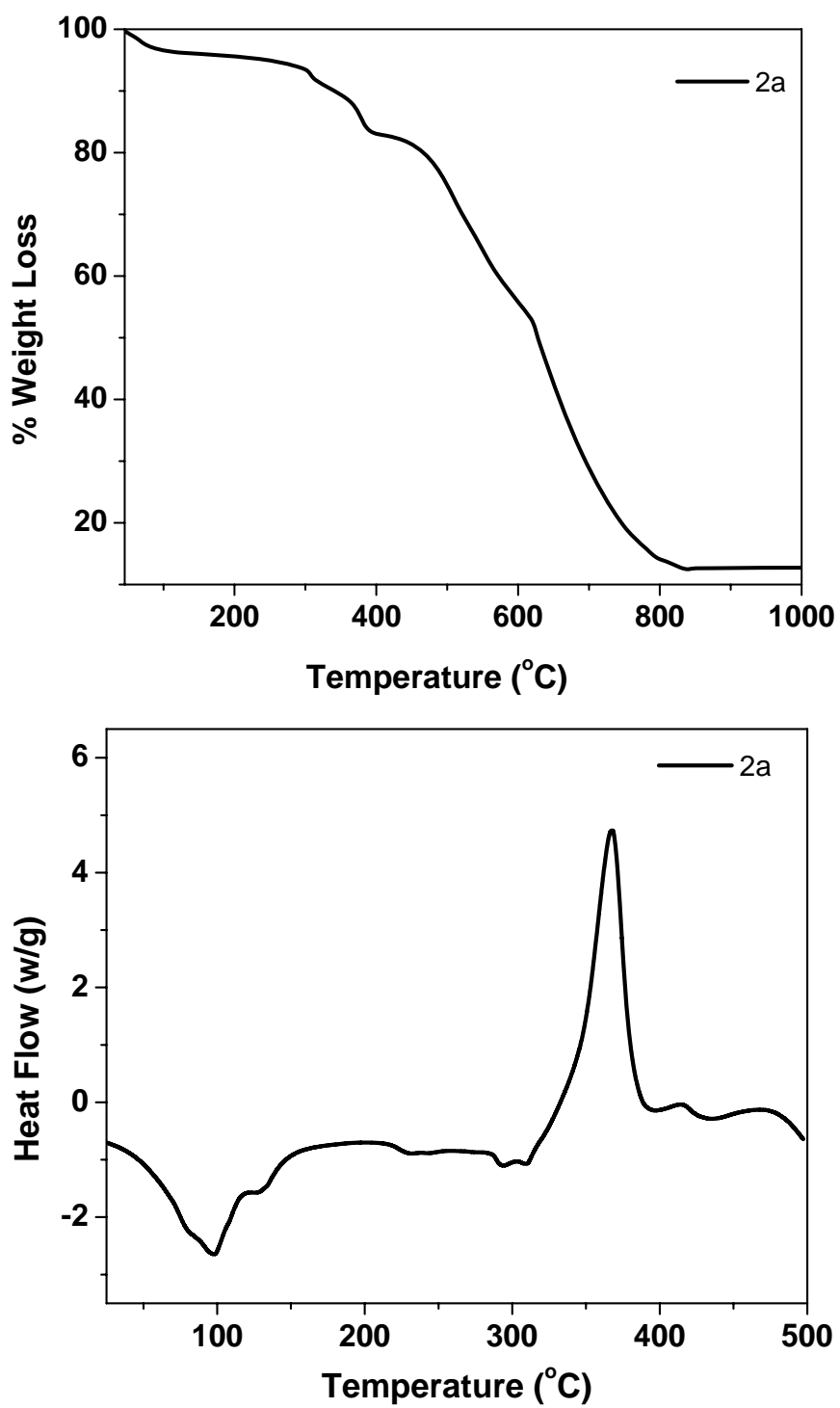


Figure S6. TGA (upper) and DSC (lower) plots for complex 2a.

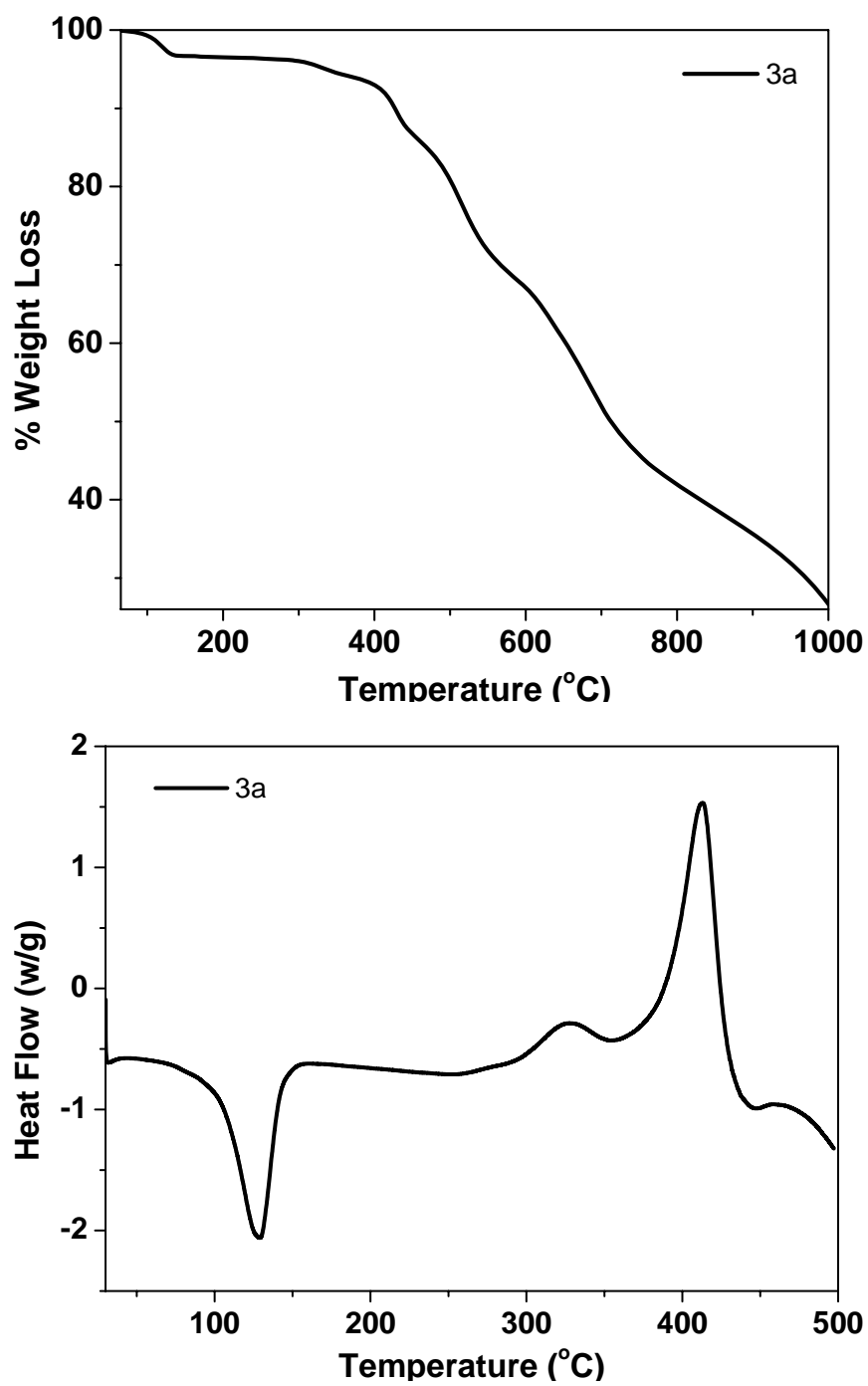


Figure S7. TGA (upper) and DSC (lower) plots for complex 3a.

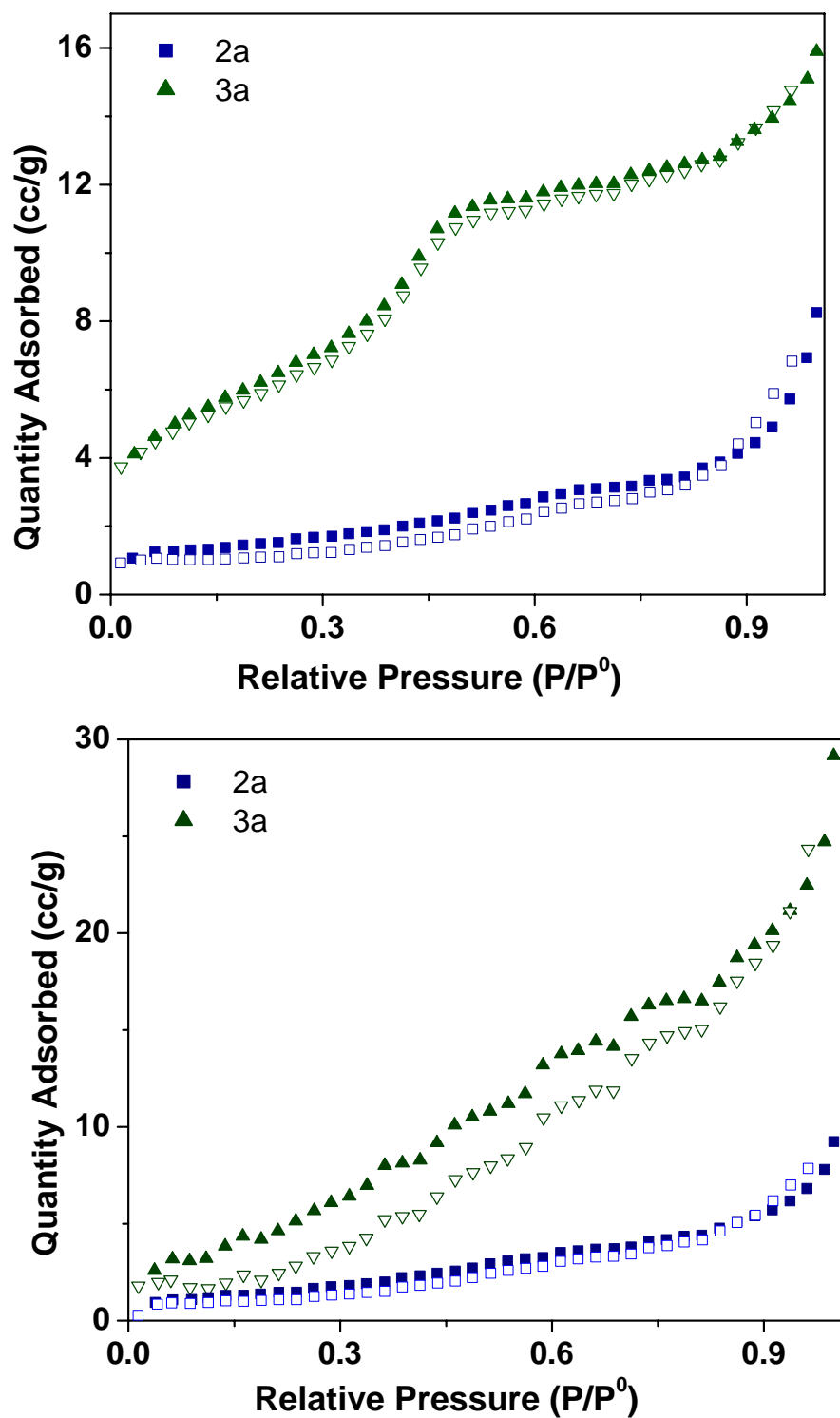


Figure S8. Gas adsorption isotherms measured at 77 K (upper) and at 298 K (lower) for networks **2a** and **3a**. Filled and open symbols denote the sorption and desorption, respectively.

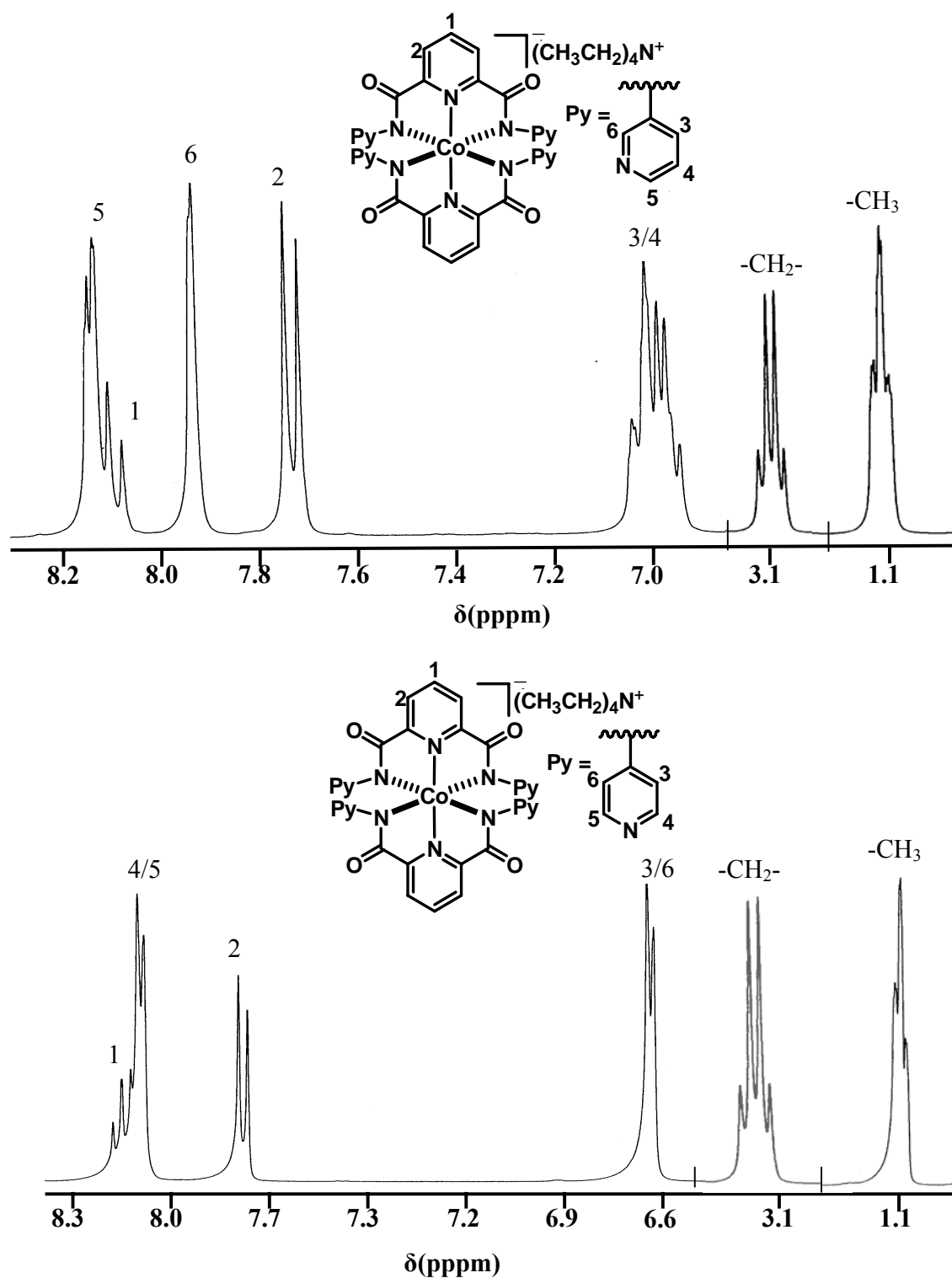


Figure S9. ¹H NMR spectra of complexes, Et₄N[Co(L²)₂] (**2**) (upper) and Et₄N[Co(L³)₂] (**3**) (lower) in [D₆]DMSO.

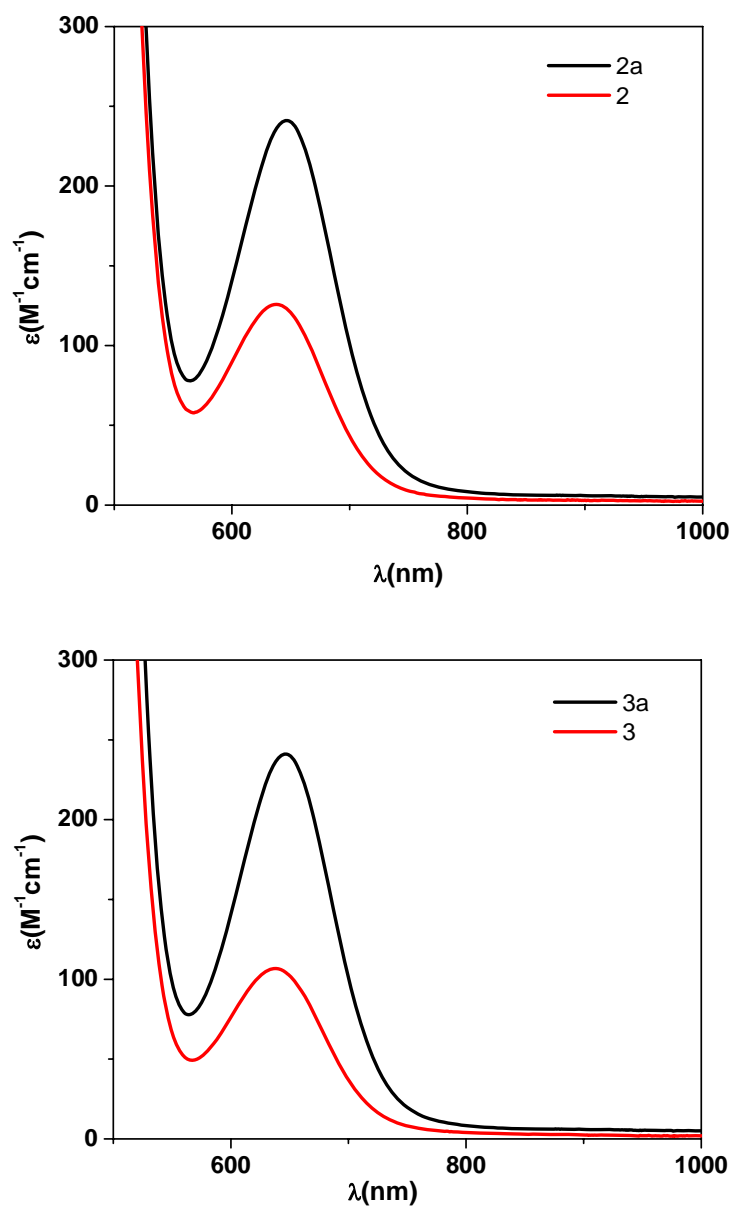


Figure S10. Absorption spectra of complexes **2** and **2a** (upper) and **3** and **3a** (lower) in DMSO.