Three *p*-tert-Butylthiacalix[4]arene-supported Cobalt Compounds Obtained in One Pot Involving in situ Formation of N_6H_2 Ligand

Yanfeng Bi,[†, §] *Wuping Liao,*[†,*] *Guancheng Xu,*[‡] *Ruiping Deng,*[†] *Meiyan Wang,*[†, §]

Zhijian Wu,[†] *Song Gao,*[‡] *and Hongjie Zhang*[†,*]

[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

[‡]Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[§]Graduate School of Chinese Academy of Sciences, Beijing 100049, China

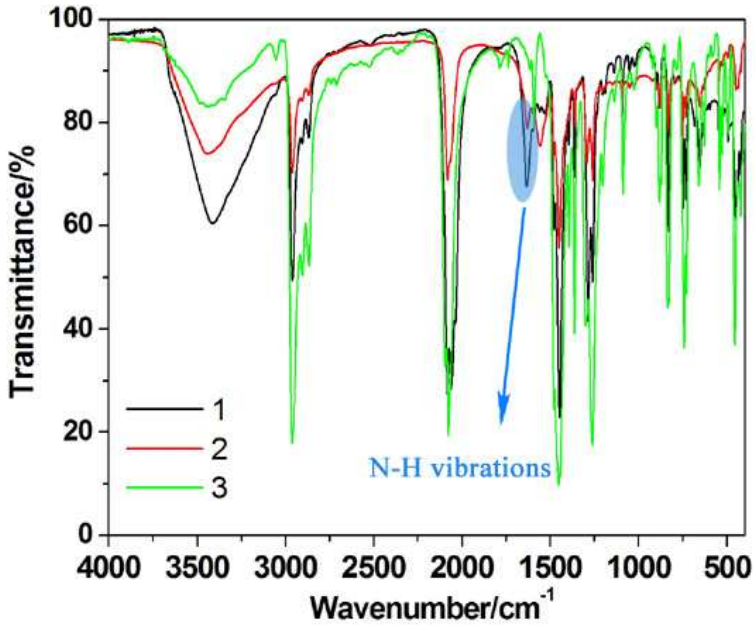

Figure S1. FTIR spectra of compounds **1-3.** N-H stretching absorption bands of -NH_2 group are observed at *ca.*1633 cm^{-1} in **1** and **2**.

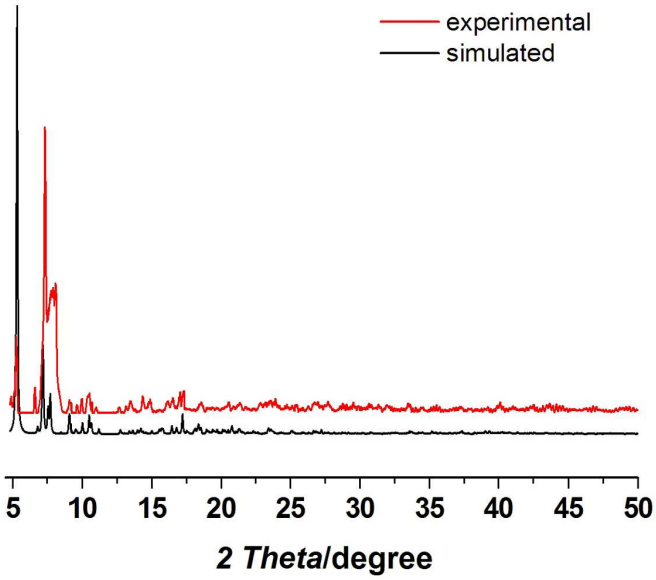

Figure. S2. Simulated (black) and experimental (red) XRD patterns of **1**. Slight differences may arise from the lost of solvent molecules at room temperature.

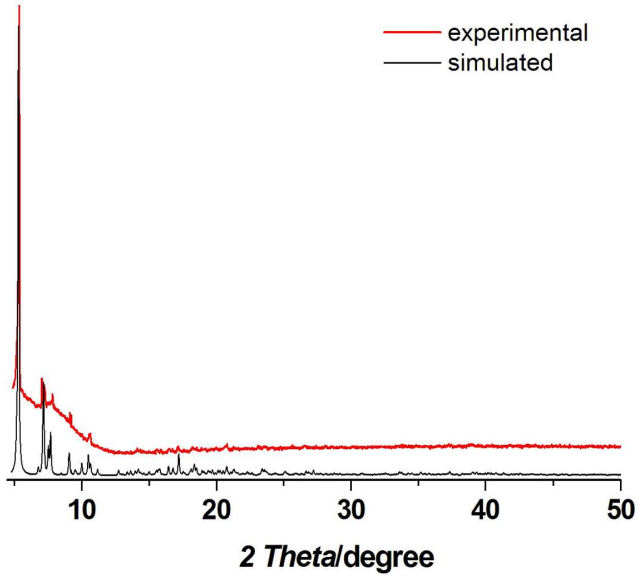

Figure. S3. Simulated (black) and experimental (red) XRD patterns of **3**. Slight differences may arise from the lost of solvent molecules at room temperature.

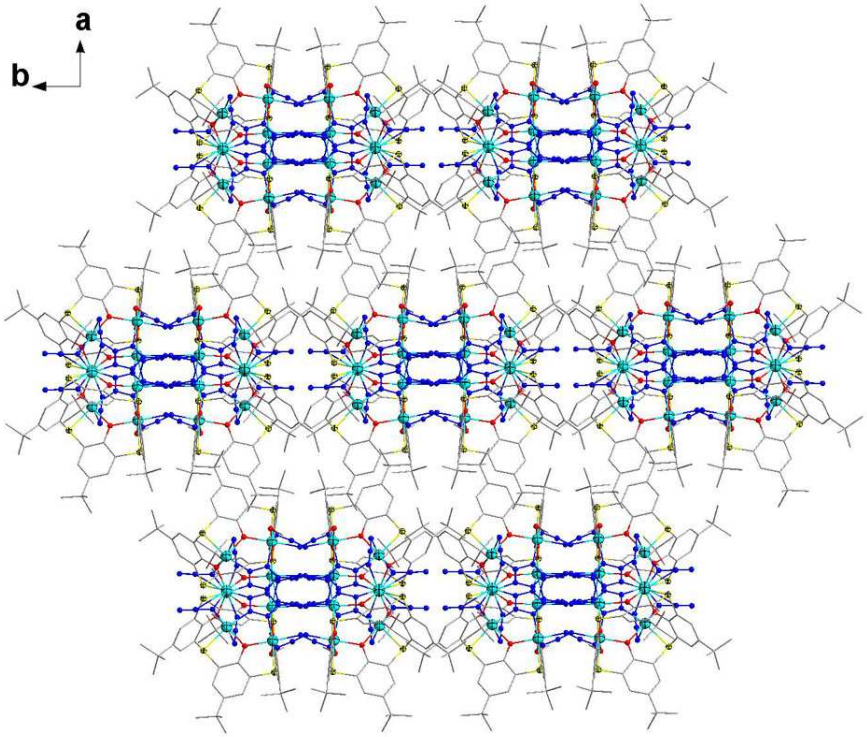

Figure S4. Extended structure of compound **1** showing one chain surrounded by six neighbors.

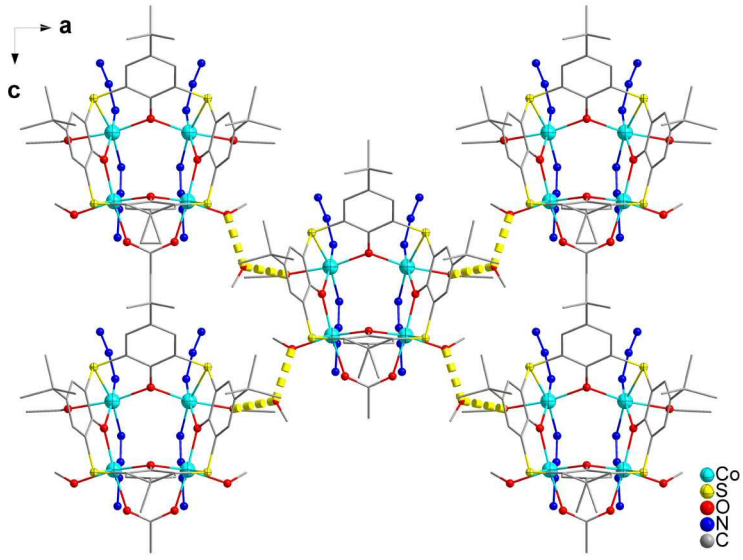

Figure S5. Representation of one octanuclear unit surrounded by four others through C–H···O/N hydrogen bonds in **2**. Yellow doted lines show hydrogen bonds.

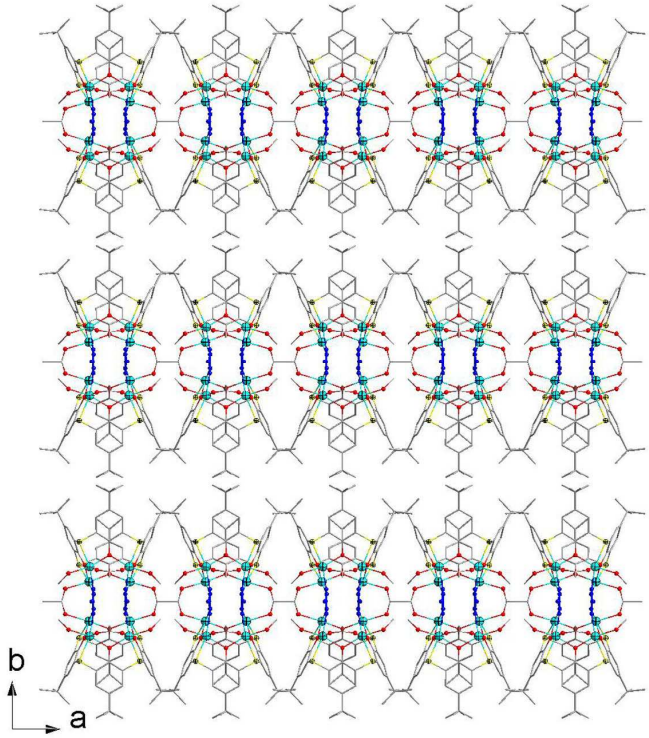

Figure S6. View of the extended structure of compound **2**.

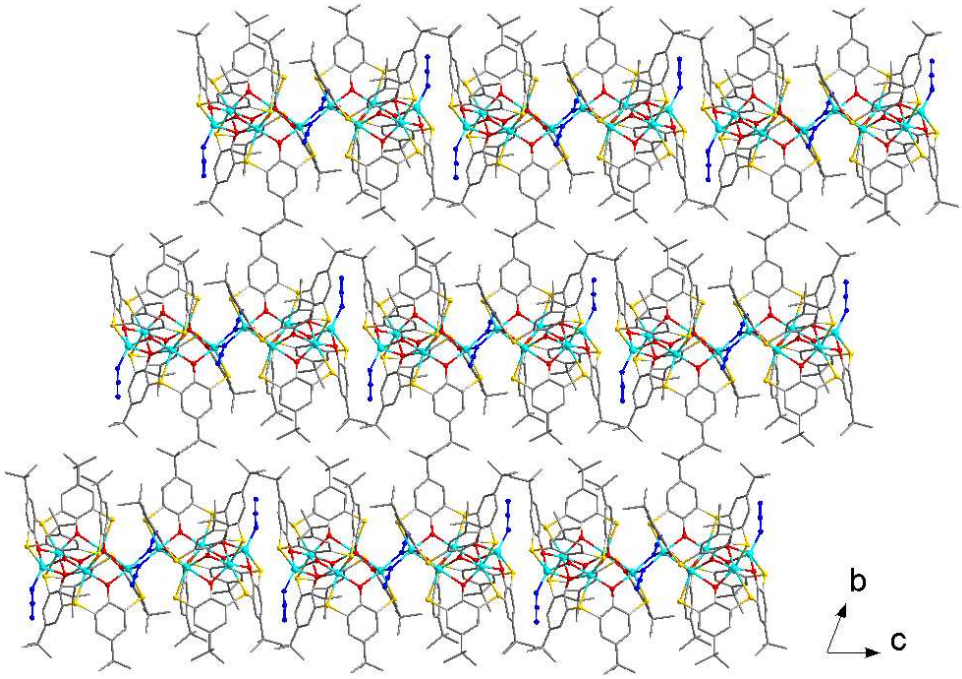

Figure S7. View of the extended structure of compound **3**.

Thermal Gravimetric (TG) experiments

The samples of **1** (1.85mg) and **3** (2.37 mg) were left in air to a stable weight and then used for TG measurements in N_2 at a heating rate of 10 °C min^{-1}.

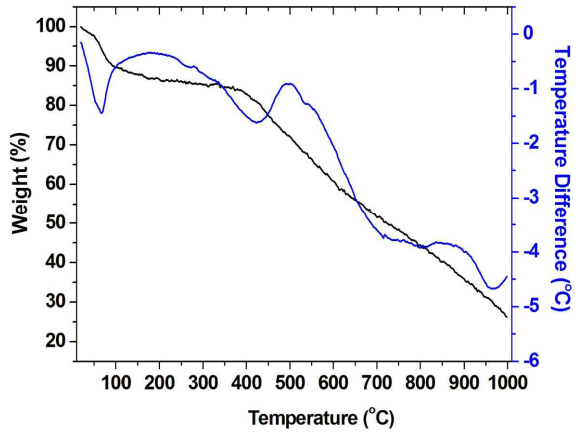

Figure S8. TGA/DTA curves of **1**.

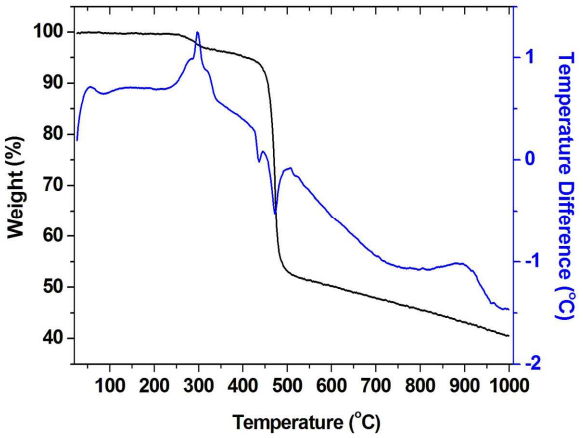

Figure S9. TGA/DTA curves of **3**.

Table S1. Selected bond distances (Å) and angles (º) for compounds **1-3**.

Compound-1				**Compound-2**	
Co(1)-O(1)	2.050(4)	Co(3)-O(3)	2.029(4)	Co(1)-O(1)	2.068(4)
Co(1)-N(13	2.052(8)	Co(3)-O(2)	2.055(3)	Co(1)-O(2)	2.081(3)
Co(1)-O(4)	2.114(4)	Co(3)-N(4)	2.062(4)	Co(1)-N(2)	2.096(4)
Co(1)-N(2)	2.119(5)	Co(3)-N(7)	2.065(4)	Co(1)-O(5)	2.076(5)
Co(1)-O(5)	2.260(10)	Co(3)-S(3)	2.4055(15)	Co(1)-O(6)	2.081(15)
Co(1)-S(1)	2.4224(17)	Co(3)-N(12)	2.416(7)	Co(1)-S(1)	2.4534(13)
Co(2)-O(1)	2.032(4)	Co(4)-O(3)	2.040(4)	Co(2)-O(1)	2.057(3)
Co(2)-N(7)	2.053(4)	Co(4)-O(4)	2.072(4)	Co(2)-N(1)	2.064(5)
Co(2)-O(2)	2.089(4)	Co(4)-N(16)	2.077(8)	Co(2)-N(5)	2.082(4)
Co(2)-N(3)	2.090(4)	Co(4v-N(5)	2.105(5)	Co(2)-O(3)	2.094(2)
Co(2)-N(10)	2.388(5)	Co(4)-N(18)[a]	2.170(18)	Co(2)-O(4)	2.249(5)
Co(2)-S(2)	2.4112(16)	Co(4)-S(4)	2.4245(18)	Co(2)-S(2)	2.4157(15)
Co(2)-O(1)-Co(1)		121.45(18)		Co(2)-O(1)-Co(1)	120.61(17)
Co(3)-O(2)-Co(2)		125.17(16)		Co(1)-O(2)-Co(1)[a]	117.5(2)
Co(2)-N(7)-Co(3)[a]		120.7(2)		Co(2)-O(3)-Co(2)[a]	124.5(2)
Co(3)-O(3)-Co(4)		120.82(19)		Co(2)-N(5)-Co(2)[b]	117.8(3)
Co(4)-O(4)-Co(1)		124.56(19)			
Compound-3					
Co(1)-O(5)	1.973(2)	Co(2)S(6)	2.4698(10)	Co(4)-O(7)	2.066(3)
Co(1)-O(4)	2.026(2)	Co(3)-O(7)	1.984(3)	Co(4)-O(8)	2.134(2)
Co(1)- O(1)	2.188(2)	Co(3)-O(6)	1.988(2)	Co(4)-S(8)	2.4740(10)
Co(1)-O(8)	2.201(2)	Co(3)-O(1)	2.100(2)	Co(4)-S(3)	2.6478(10)
Co(1)-S(5)	2.5810(10)	Co(3)-O(2)	2.214(2)	Co(5)-N(4)	1.931(4)
Co(1)-S(1)	2.6244(10)	Co(3)-S(2)	2.4532(10)	Co(5)-O(4)	1.936(2)
Co(2)-O(6)	2.012(3)	Co(3)-S(7)	2.7598(10)	Co(5)-O(3)	1.942(2)
Co(2)-O(5)	2.022(2)	Co(4)-O(2)	2.015(3)	Co(5)-O(8)	2.274(3)
Co(2)-N(1)	2.079(3)	Co(4)-O(3)	2.033(2)	Co(5)-S(4)	2.4619(10)
Co(2)-O(1)	2.303(2)				
Co(3)-O(1)-Co(1)	112.24(10)	Co(5)-O(4)-Co(1)	109.92(11)	Co(4)-O(8)-Co(5)	92.07(9)
Co(2)-O(1)-Co(2)	95.87(9)	Co(1)-O(5)-Co(2)	112.31(11)	Co(1)-O(8)-Co(5)	92.91(9)
Co(1)-O(1)-Co(2)	95.24(9)	Co(3)-O(6)-Co(2)	109.74(11)	Co(1)-N(1)-Co(2)[a]	92.91(9)
Co(4)-O(2)-Co(3)	99.42(10)	Co(3)-O(7)-Co(4)	105.71(11)		
Co(5)-O(3)-Co(4)	105.95(11)	Co(4)-O(8)-Co(1)	119.06(11)		

a: -x,-y,1-z for **1**; a: 1-x,y,z; b: x,1-y,z for **2**; a: -x,1-y,1-z for **3**.