

## Supporting Information

for

### **Topological Variability of Zn(II) and Co(II) 3D Metal–Organic Frameworks Obtained Through Solvothermal in Situ Disulfide Cleavage**

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## Experimental

### General methods

All starting materials used in these synthetic reactions are purchased commercially and were used as obtained from the supplier. IR (KBr pellets) spectra were recorded on powdered samples with PerkinElmer Spectrum One instrument. Luminescent data were obtained from an Horiba Jobin Yvon Fluorolog-3 spectrometer on solid crystalline samples at room temperature. The CD (KCl) spectra were recorded on a MOS 450 spectropolarimeter (Bio Logic). Thermogravimetric analysis was recorded using a NETZSCH STA 449C unit at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. Elemental analyses of C, H, N and S were performed on a Vario EL III CHNOS analyzer. Powder X-ray diffraction (PXRD) patterns were recorded by a RIGAKU DMAX2500 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Magnetic susceptibility data were measured using a Quantum Design MPMS-XL5 SQUID magnetometer.

### Syntheses of complexes **1-2**

[Zn(2-sb)(4,4'-bpy)]<sub>n</sub>·0.5nDMF·2nH<sub>2</sub>O (**1**). Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (30mg, 0.1mmol), 4,4'-bpy (16mg, 0.1mmol), H<sub>2</sub>dtb (15mg, 0.05mmol) were dissolved in 2ml of mixed solvents of N,N-dimethylformamide (DMF) and EtOH (1:1,v/v) and heated in a 25ml beaker at 85 °C for 1 day. Dark yellow crystalline blocks that formed was collected, washed with H<sub>2</sub>O, and dried in the air. Yield: 51% based on Zinc. Elem anal. Calcd for 1: C 44.95; H 3.98; N 7.08; S 6.49. Found: C 45.05; H 3.88; N 7.34; S 6.48. IR (KBr, cm<sup>-1</sup>) : 3566s, 1614m, 1396m, 746w.

[Co(2-sb)(4,4'-bpy)(H<sub>2</sub>O)]<sub>n</sub>·nDMF (**2**). Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (30mg, 0.1mmol), 4,4'-bpy (16mg, 0.1mmol), H<sub>2</sub>dtb (15mg, 0.05mmol), HNO<sub>3</sub> (2 drops, 0.5M) were dissolved in 2ml DMF and heated in a 25ml beaker at 85 °C for 1 day. Red crystalline blocks that formed was collected, washed with H<sub>2</sub>O, and dried in the air. Yield: 38% based on Cobalt. Elem anal. Calcd for 2: C 47.44; H 4.17; N 8.29; S 6.33. Found: C 47.25; H 4.13; N 8.13; S 6.44. IR (KBr, cm<sup>-1</sup>) : 3566s, 1648m, 1400m, 770w.

### X-Ray crystallography

Diffraction data for **1** and **2** were collected on a Rigaku SCXmini CCD instrument, with graphite monochromated Mo-K $\alpha$  radiation. The structures were solved using direct methods and refined on F<sup>2</sup> using SHELXTL<sup>1</sup>. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model. Selected bond distances and angles of the complexes are listed in Table S1.

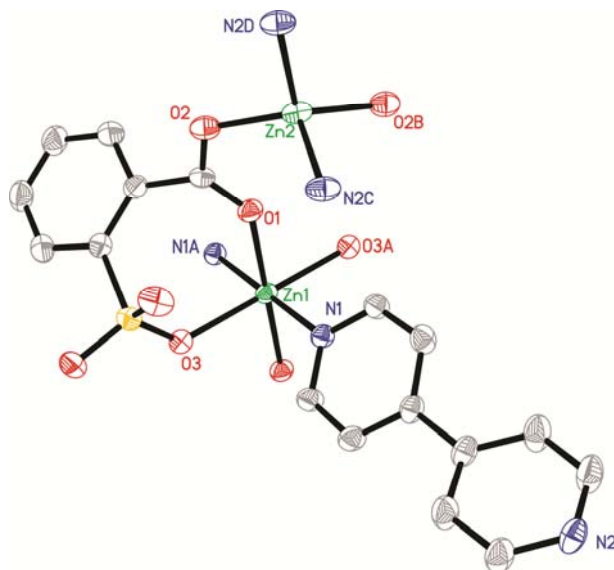


Fig. S1 Coordination environment of **1** with thermal ellipsoids shown at 30%.  
(symmetry code: A  $1-x, 1-y, -z$ ; B  $3/4-x, 3/4-y, z$ ; C  $x, 5/4-y, 1/4-z$ ; D  $3/4-x, y-1/2, 1/4-z$ )

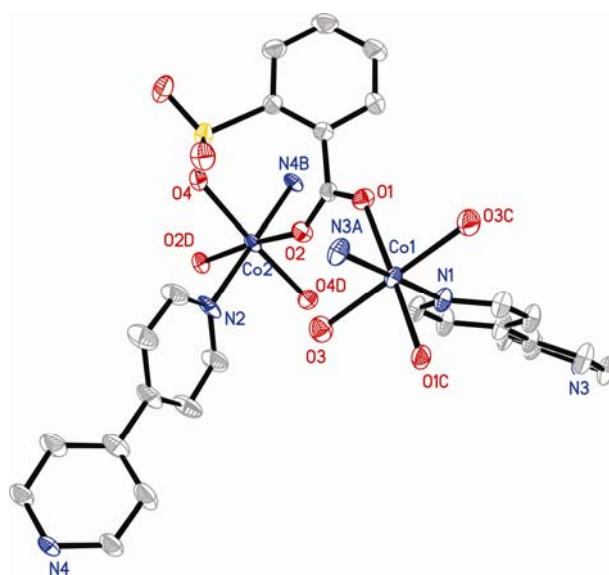


Fig. S2 Coordination environment of **2** with thermal ellipsoids shown at 30%.  
(symmetry code: A  $x, y-1, z$ ; B  $1+x, 1+y, z$ ; C  $-x, -x+y, 5/3-z$ ; D  $y-1, 1+x, 2-z$ )

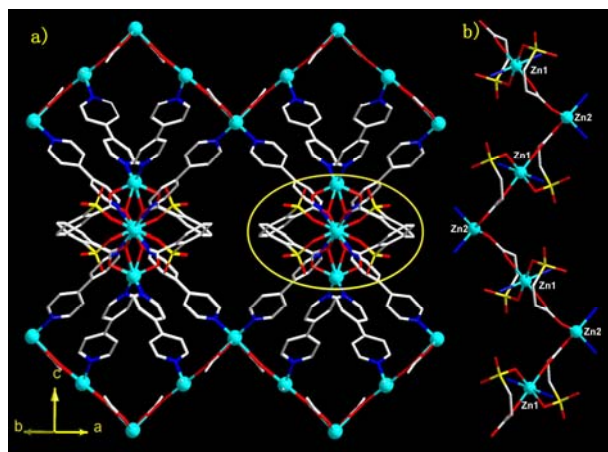


Fig. S3 (a) Perspective view of the 3D framework of **1**. (b) Coordination environment (yellow circle in the figure) of the carboxylate chain. (Color code: carbon: gray; nitrogen: blue; oxygen: red; sulfur: yellow; zinc: turquoise). Zinc atoms are shown in ball mode, the others are shown in stick mode.

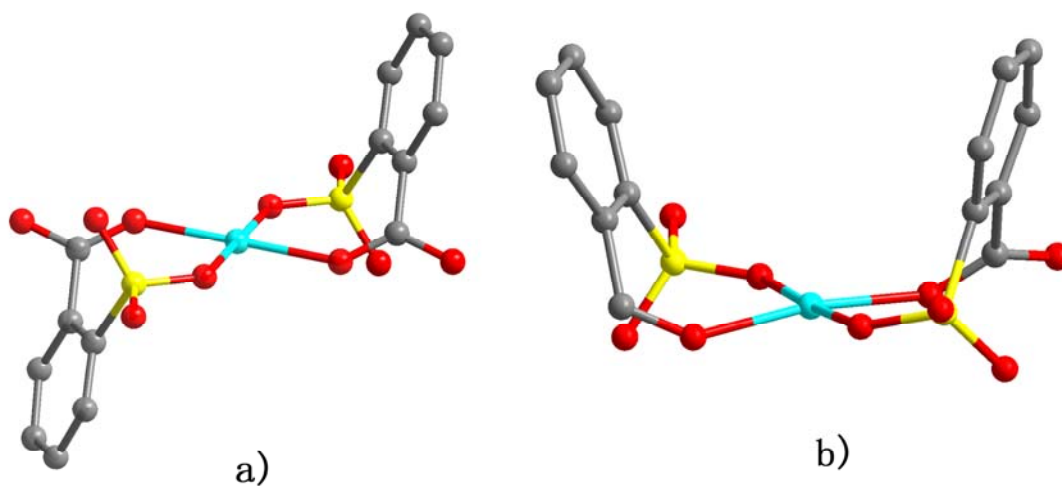


Fig. S4 View of chair (a) and boat (b) conformations of the 2-sulfobenzoic acid ligand

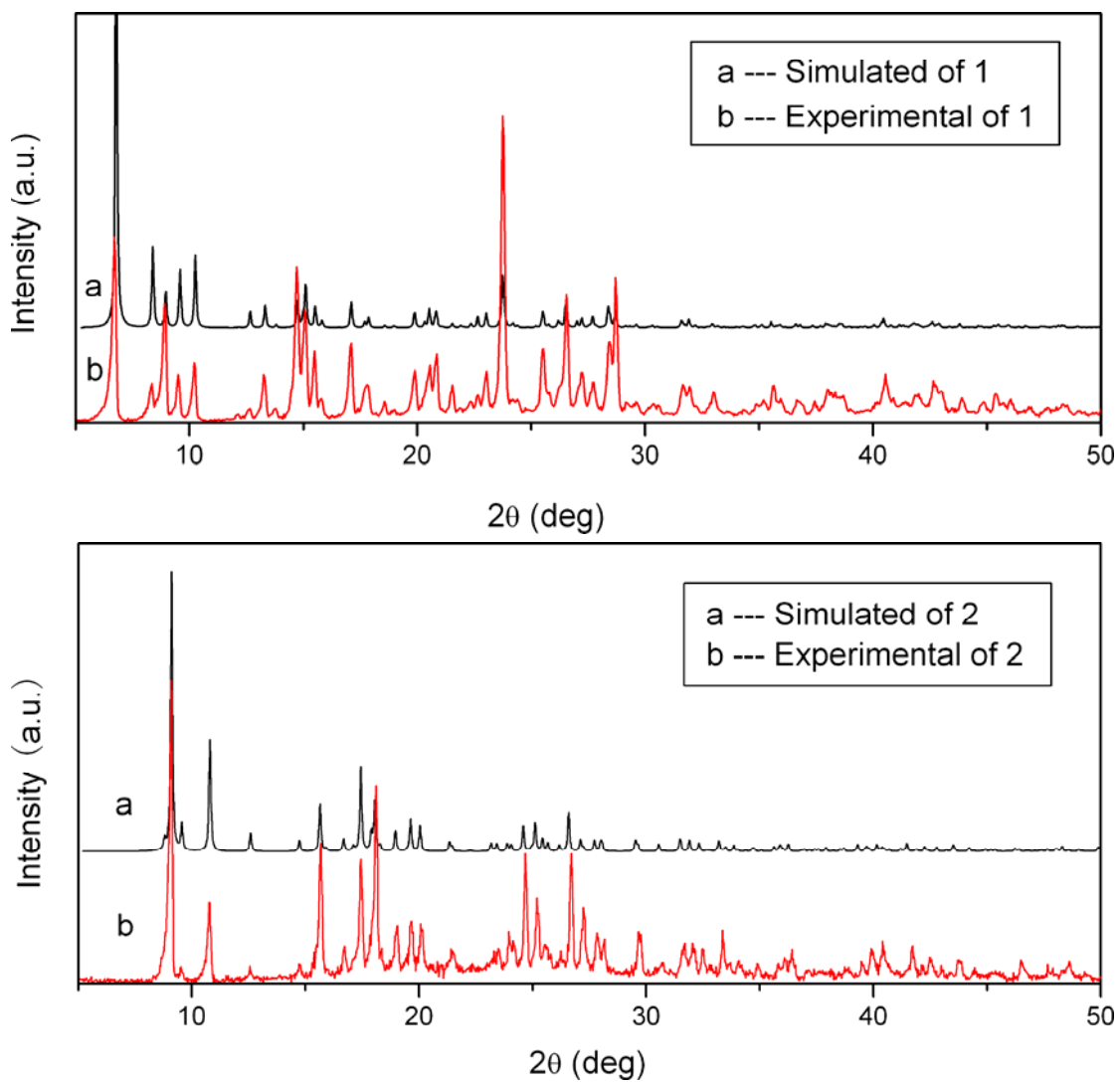


Fig. S5 X-Ray powder diffraction patterns of **1** and **2**.

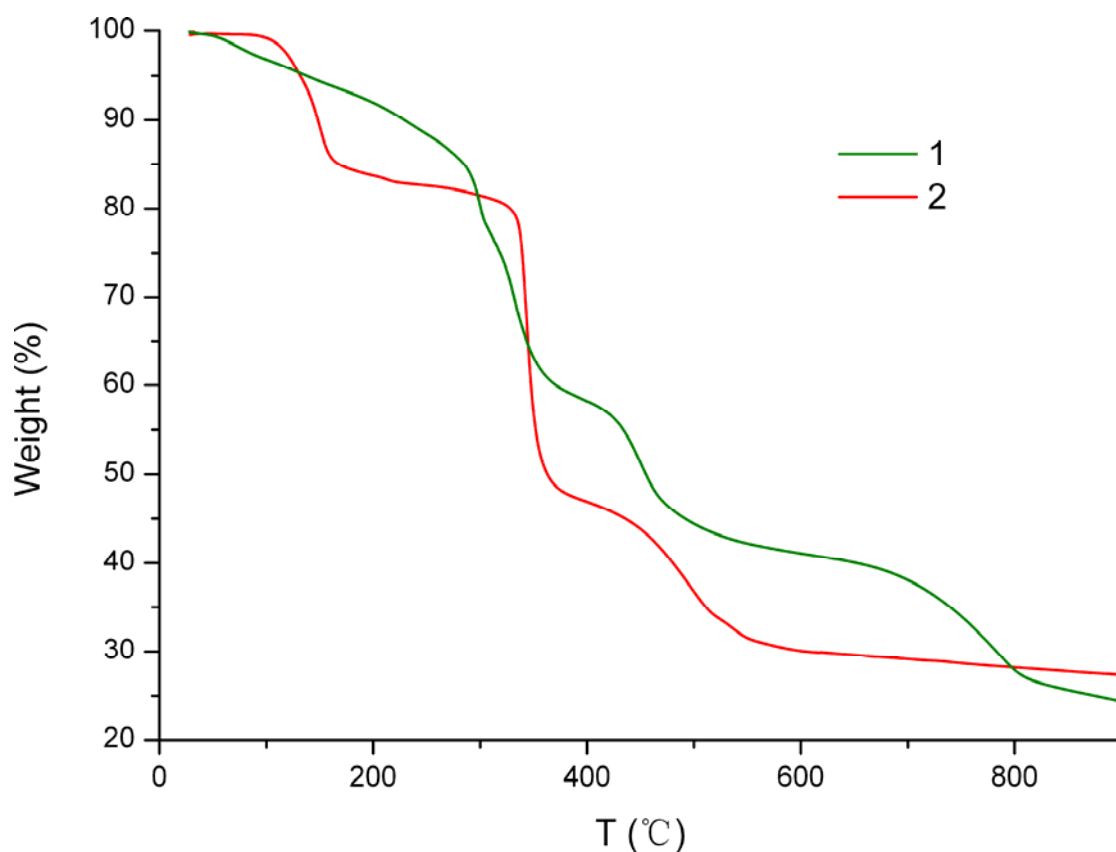


Fig. S6 TGA curve for complexes **1** and **2**.

As shown in Figure S6, complex **1** underwent a 14.7% mass decrease between ~30 and ~280 °C, corresponding to the elimination of its free water and DMF molecules in the channels of the framework (14.6% predicted). And the residue composition of this complex is then decomposed in the temperature arrange of ~280 to ~800 °C.

For complex **2**, TGA curve indicates that the free DMF molecules are lost firstly (absd 14.02%, calcd 14.44%) from ~100 to ~160 °C followed by water molecules of crystallization (absd 3.95%, calcd 3.62%) from 170 to 330 °C.

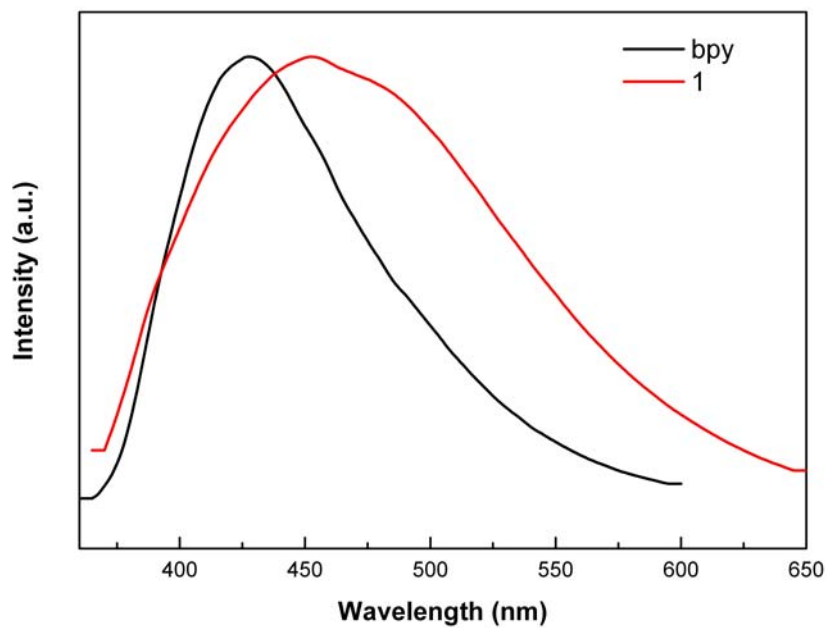


Fig. S7 Photoluminescent emission spectrum for **1** in the solid state at room temperature.

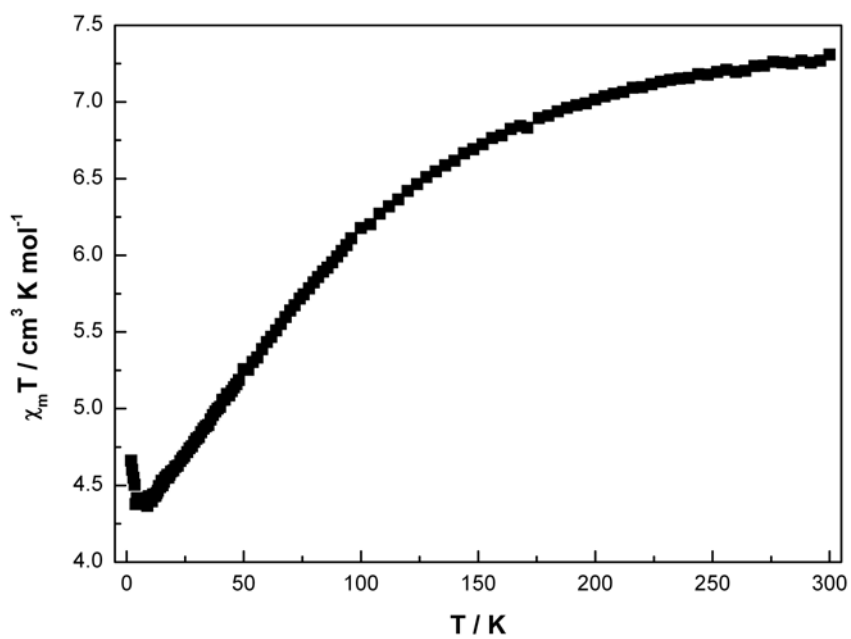


Fig. S8 Temperature dependence of the  $\chi_m T$  product for **2**.

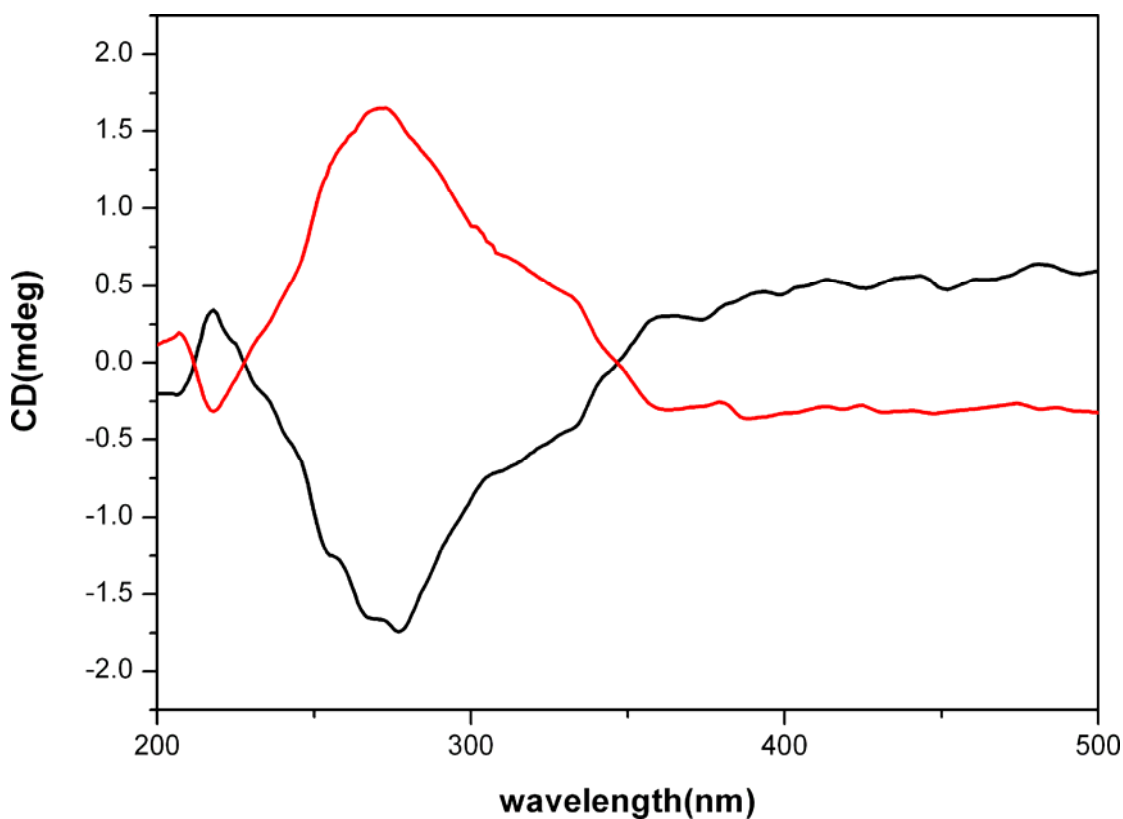


Fig. S9 Different solid state CD spectra (black and red) of complex 2.

Table S1. Selected bond lengths ( $\text{\AA}$ ) and angles (deg) for complexes **1** and **2**

<b>Complex 1</b>			
Zn1—N1	2.090 (2)	Zn2—O2	1.945 (3)
Zn1—O1	2.131 (2)	Zn2—N2 <sup>iii</sup>	2.047 (3)
Zn1—O3	2.162 (2)		
N1—Zn1—O1	88.27 (9)	O2—Zn2—O2 <sup>ii</sup>	132.47 (15)
N1—Zn1—O3	89.46 (9)	O2—Zn2—N2 <sup>iii</sup>	99.51 (12)
O1—Zn1—O3	91.50 (9)	N2 <sup>iii</sup> —Zn2—N2 <sup>iv</sup>	101.54 (16)
<b>Complex 2</b>			
Co1—O1	2.085 (2)	Co2—O2	2.066 (2)
Co1—O3	2.137 (3)	Co2—O4	2.127 (3)
Co1—N1	2.153 (4)	Co2—N2	2.186 (4)
O1—Co1—O3	85.54 (10)	O2—Co2—O4	88.74 (10)
O1—Co1—N1	92.16 (7)	O2—Co2—N2	85.22 (7)
O3—Co1—N1	90.02 (8)	O4—Co2—N2	91.88 (7)

Symmetry codes for 1: (ii) 1+x, 1+y, 1+z; (iii) 1+x, y, -1+z; (iv) x, 5/4-y, 1/4-z.

## Reference

1 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution and Refinement*, 1997, University of Göttingen.