Supplementary Material (ESI) for Chemical Communications

Magnetic Canting or Not? Two Isomorphous 3D Co^{II} and Ni^{II} Coordination Polymers with the Rare Non-interpenetrated (10,3)-d Topological Network, Showing Spin-canted Antiferromagnetism Only in the Co^{II} System

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Materials, Methods, Syntheses and Characterizations

All the reagents for synthesis were obtained commercially and used as received. 3,4-Dicyano-1,2,5-thiadiazole (DCT) was synthesized by following a reported procedure [Ribaldone, G.; Grecu, R. *German Pat.* 2651604, 1977 (*Chem. Abstr.,* 1977, **87**, 135344)].

Elemental analyses were performed on a Perkin-Elmer 240C analyzer. IR spectra were measured on a TENSOR 27 (Bruker) FT-IR spectrometer with KBr pellets. Thermal analyses were performed in the temperature range of 25~600 °C on a Rigaku standard TG-DTA analyzer in N_2 with an increasing temperature rate of 10 °C/min^{-1}. An empty Al_2O_3 crucible was used as reference. The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra was carried out by the single-crystal data and diffraction-crystal module of the commercially available *Cerius2* program (*Cerius2*, Molecular Simulation Incorporated, San Diego, CA, 2001.).

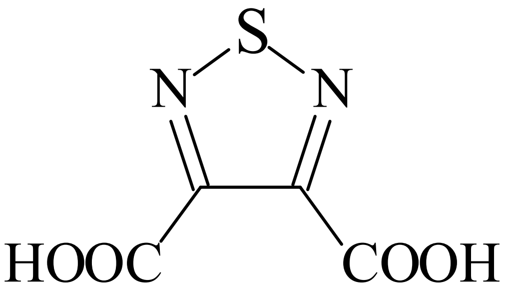
The two complexes are very stable in air at ambient temperature and have high thermal stability with decomposing above 300 °C. They are almost insoluble in common solvents such as water, alcohol, acetonitrile, chloroform, acetone and toluene. XRPD patterns (Fig. 1S), IR spectra (Figure 2S), TG-DTA profiles (Figure 3S) are shown below.

Single-crystal X-ray diffraction measurements for **1** and **2** were carried out on a Rigaku R-AXIS RAPID IP diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. Data collections and cell refinement were performed with RAPID-AUTO (Rigaku. *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan, 2004). Data reduction was carried out using CrystalStructure (Rigaku/MSC. CrystalStructure. Rigaku/MSC Inc. The Woodlands, Texas, USA, 2004). The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL (Sheldrick, G. M., *SHELXTL Version 6.1. Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, 1998). The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. Water H atoms were located from difference maps and refined with an O---H distance restraint of 0.85(1) Å. It should be pointed out that the two complexes crystallized in the chiral space group ($P2_1$) and the refined Flack parameters is –0.002(1) and 0.01(1), respectively. However, the examination of the atom coordinates shows that the Ni^{II} complex is the inverse of the Co^{II} complex, which shows that the pair of structures seems to be considered to be "isomorphous enantiomers". Indeed, the crystals chosen for X-ray were selected entirely at random, and presumably the bulk of each sample includes equal numbers of each enantiomer. Thus, the bulk of the two samples are isomorphous, it just happens that the two crystals selected for study were enantiomers.

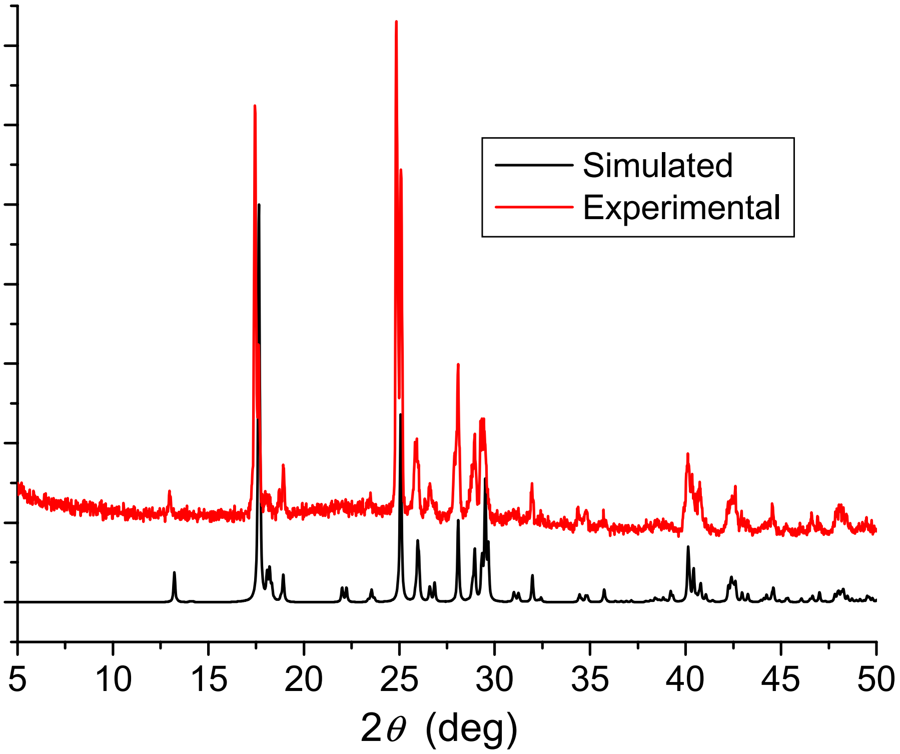
Crystallographic data (excluding structure factors) for the structures **1** and **2** have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-626633 & 626634. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (.44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Magnetic measurements were carried out in the “Servei de Magnetoquímica (Universitat de Barcelona)” on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer working in the 2~300 K range.

Chart 1S



2,1,3-thiadiazole-4,5-dicarboxylic acid (H_2**L**)


Simulated
Experimental
5
10
15
20
25
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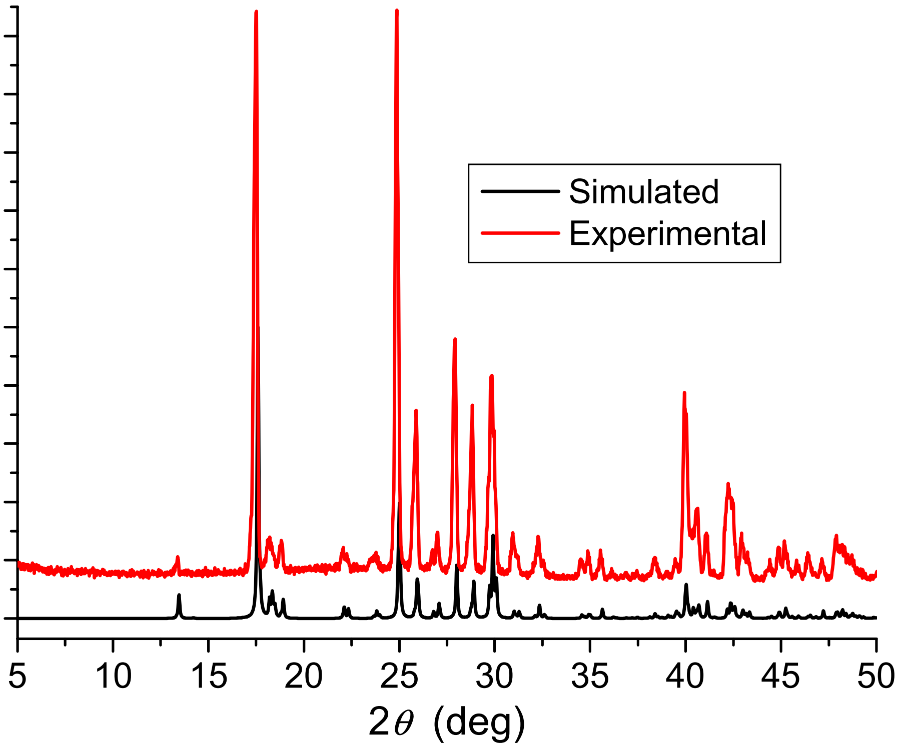
2θ (deg)

(a)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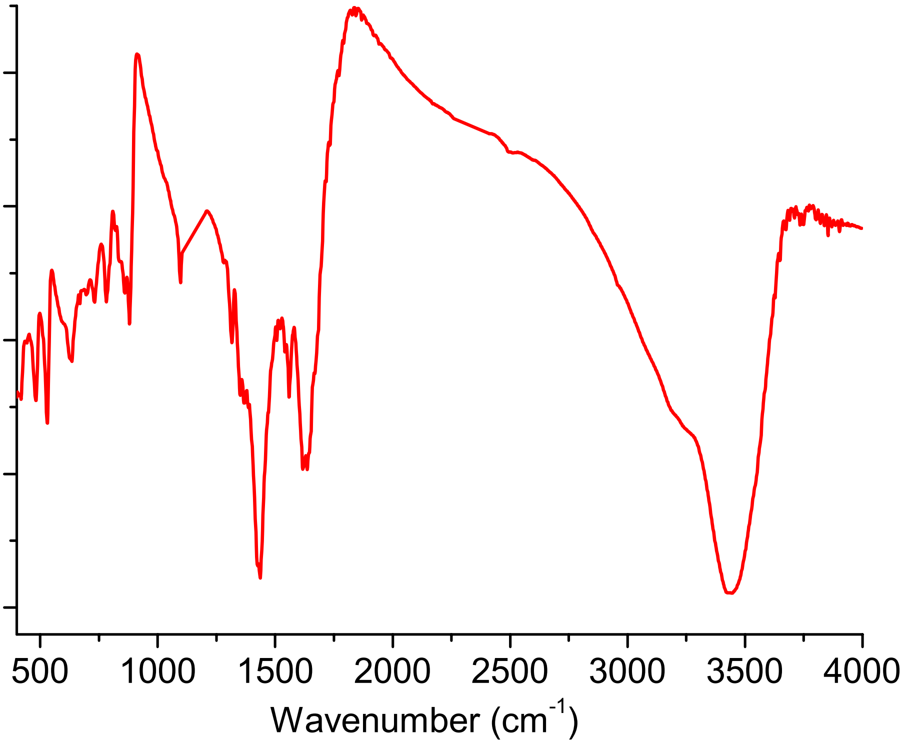
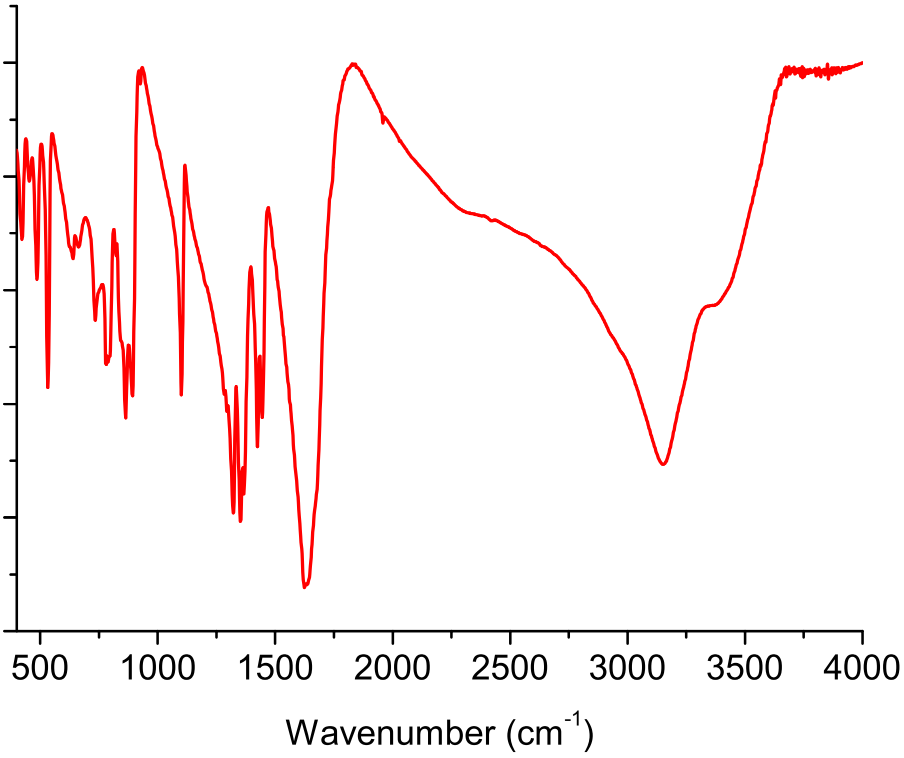
2θ (deg)

(b)

Figure 1S. XRPD patterns for **1** (a) and **2** (b).

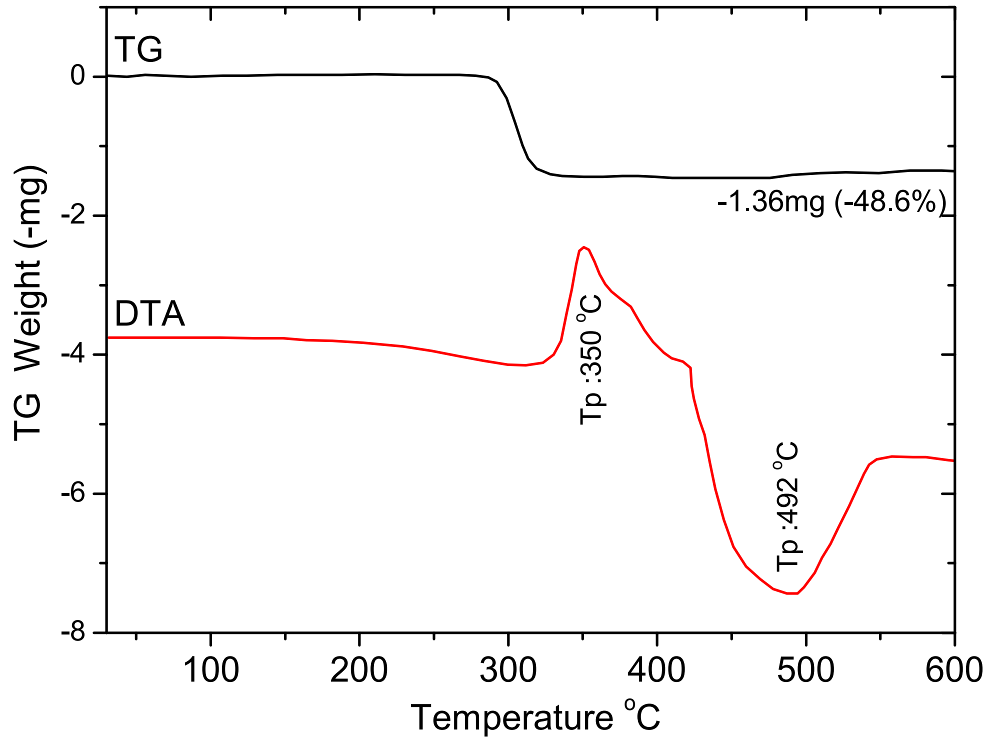


(a)

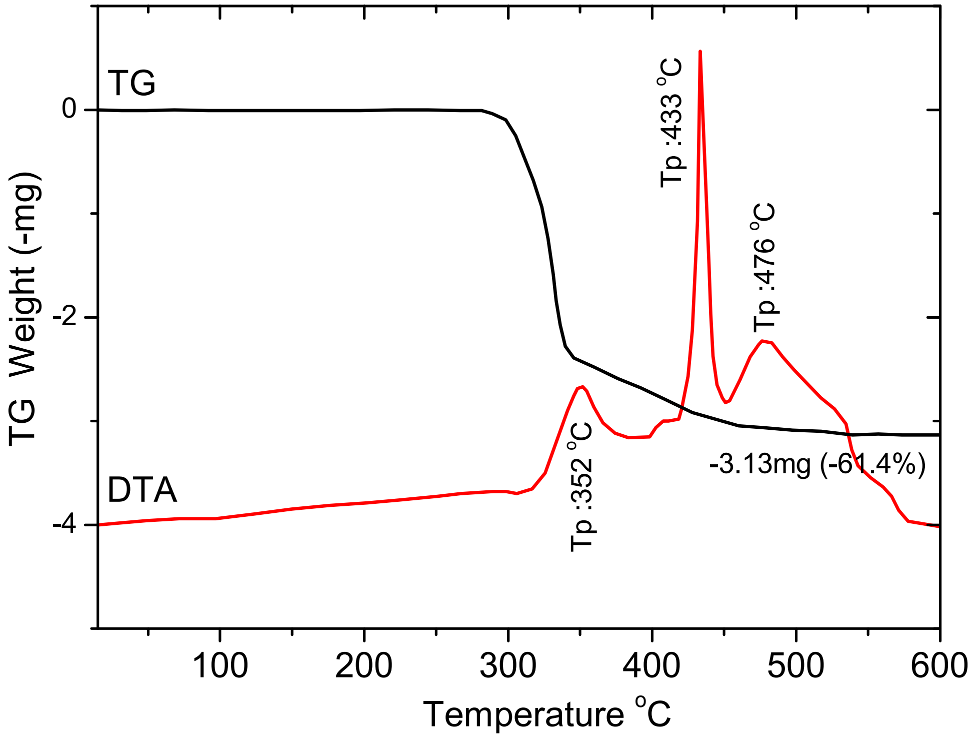


(b)

Figure 2S. FT-IR spectra of **1** (a) and **2** (b).



(a)



(b)

Figure 3S. The TG-DTA curves of **1** (a) and **2** (b).

Additional Structures

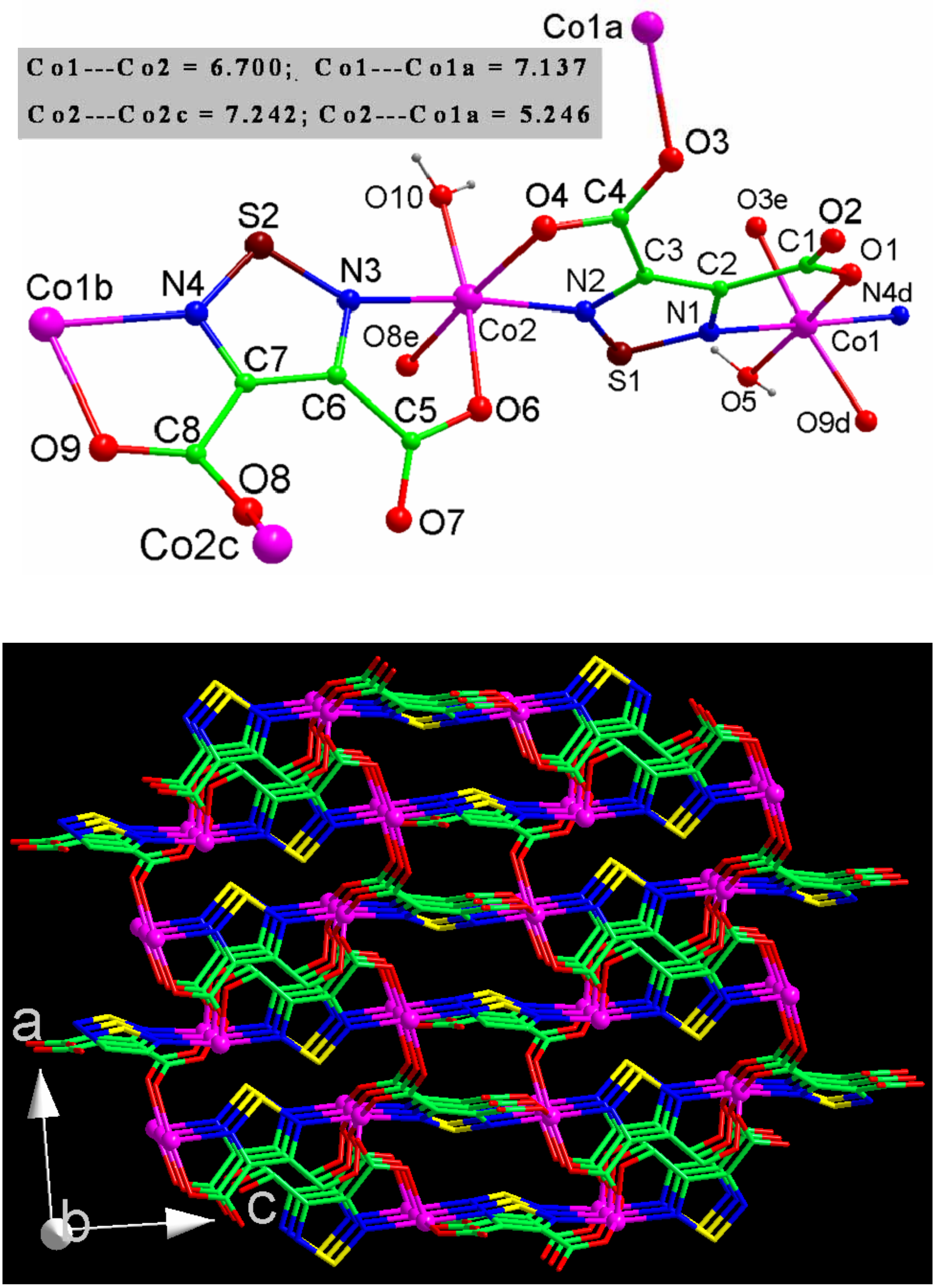


Figure 4S. Top: the local view of **1** showing the coordination situations of Co^{II} centers and the ligands (symmetry codes: a, 4 – x, 1/2 + y, 5 – z; b, x, y, z – 1; c, 3 – x, 1/2 + y, 4 – z; d, x, y, 1 + z; e, 3 – x, y

– 1/2, 4 – z); bottom: view of the overall 3-D framework of **1** (un-coordinated carboxylate O atoms and water molecules were omitted for clarity).

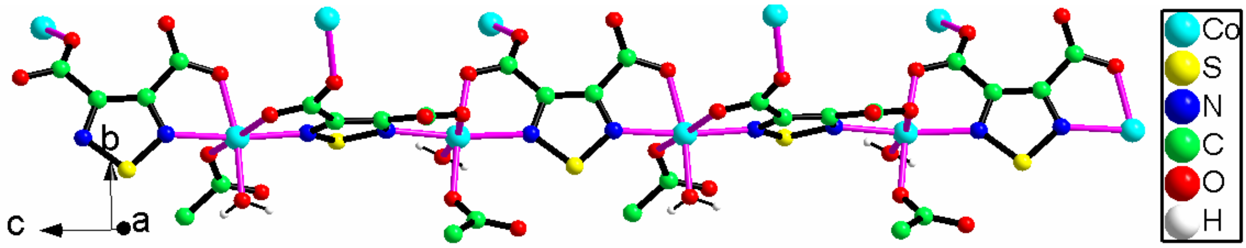


Figure 5S. View of the 1-D sub-structure in **1**.

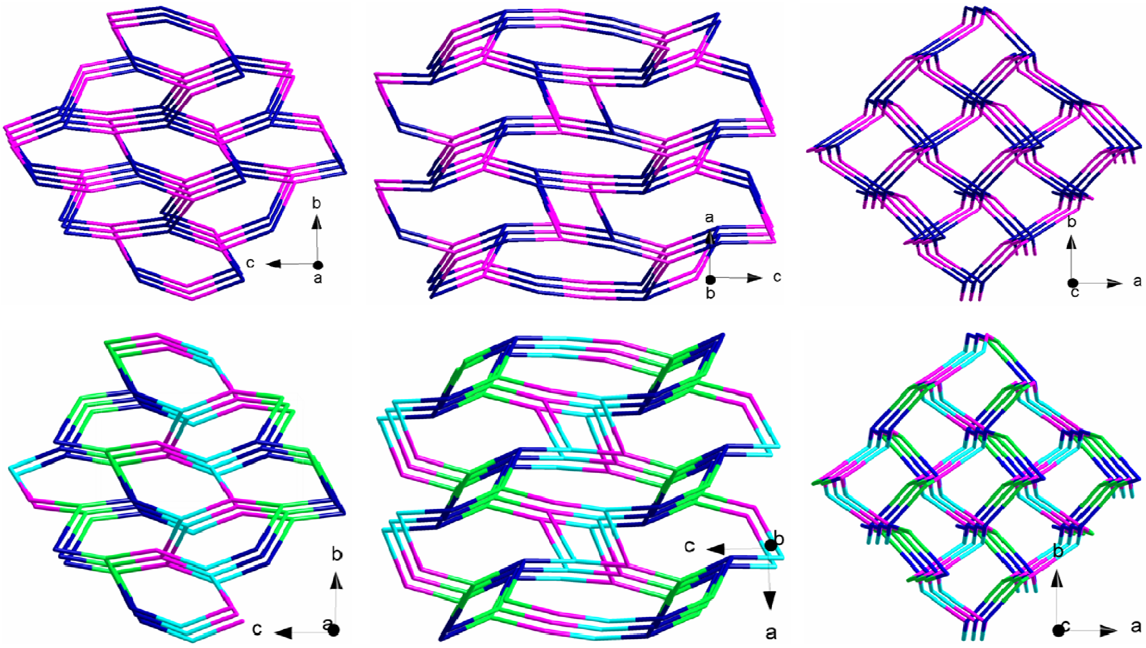


Figure 6S. The view of overall 3-connected (10,3)-d network topology of **1** along different directions, top: with all ligand nodes represented as the same pink, and all Co^{II} nodes as blue; bottom: with two crystallographically different ligands as skyey and green, and two Co^{II} nodes as pink and blue, respectively.

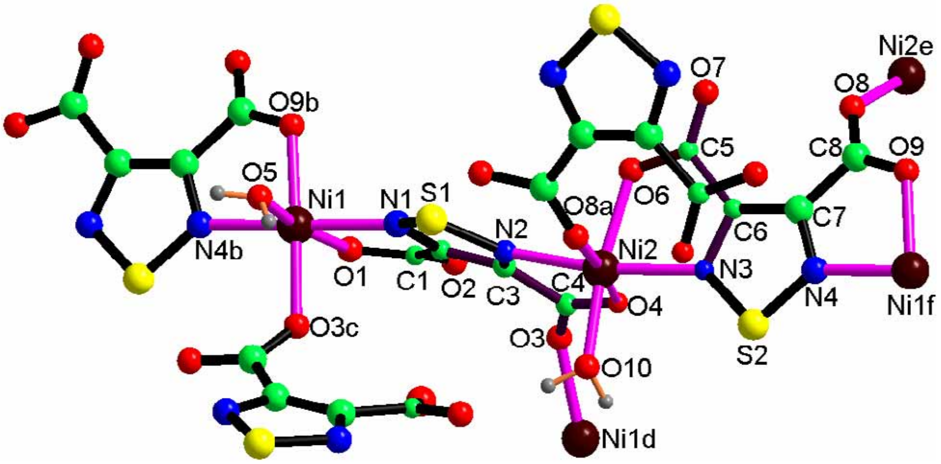


Figure 7S. The local view of **2** showing the coordination environments of $\mathrm{Ni^{II}}$ centers and ligands (symmetry codes: a, –1 – x, 1/2 + y, –2 – z; b, x, y, z – 1; c, –2 – x, 1/2 + y, –3 – z; d, –2 – x, –1/2 + y, –3 – z; e, –1 – x, –1/2 + y, –2 – z; f, x, y, z + 1). Selected distances: Ni1---Ni2 = 6.590; Ni2---Ni1d = 5.271; Ni2---Ni2e = 7.170; Ni2---Ni1f = 6.588 Å.