

Syntheses and Characterizations of Novel One-dimensional Coordination Polymers Self-assembled from $\text{Co}(\text{NCS})_2$ and Flexible Diester-bridged Pyridine-based Ligands[†]

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The self-assembly reactions of $\text{Co}(\text{NCS})_2$ with diester-bridged pyridine-based ligands $\text{pyCO}_2-(\text{CH}_2)_m-\text{O}_2\text{Cpy}$ (py = 4-pyridyl; $m = 2, 3, 4$) have been studied. Interestingly, while $\text{Co}(\text{NCS})_2$ reacted with $\text{pyCO}_2-(\text{CH}_2)_2-\text{O}_2\text{Cpy}$ (La) in MeOH/H₂O or THF/MeCN to yield two coordination polymers [$\text{Co}(\text{NCS})_2(\text{La})_2$]_n (1) and [$\text{Co}(\text{NCS})_2(\text{La})_2 \cdot 2\text{THF}$]_n (2), reactions of $\text{Co}(\text{NCS})_2$ with $\text{pyCO}_2-(\text{CH}_2)_3-\text{O}_2\text{Cpy}$ (Lb) in MeOH/MeCN and $\text{Co}(\text{NCS})_2$ with $\text{pyCO}_2-(\text{CH}_2)_4-\text{O}_2\text{Cpy}$ (Lc) in EtOH/H₂O afforded [$\text{Co}(\text{NCS})_2(\text{Lb})_2 \cdot 0.5\text{MeOH}$]_n (3) and [$\text{Co}(\text{NCS})_2(\text{Lc})_2 \cdot 2\text{H}_2\text{O}$]_n (4), respectively. The X-ray diffraction analyses indicated that polymers 1—4 consist of a one-dimensional Co(II) chain in which each of the two adjacent Co(II) ions is bridged by two $\text{pyCO}_2-(\text{CH}_2)_m-\text{O}_2\text{Cpy}$ ligands to form a macrocycle. In addition, the structures of polymers 1—4 were also characterized by infrared spectroscopy, thermogravimetry and elemental analysis.

Keywords coordination polymer, self-assembly, $\text{Co}(\text{NCS})_2$, bridged dipyridyl ligand, crystal structure

Introduction

There has been recent research interest in crystal engineering and the design of supramolecular architectures.¹ By selecting the chemical structure of ligands and the coordination geometry of transition metal ions, the organic/inorganic hybrid materials may yield a series of novel networks with various sizes and shapes of channels or cavi-

ties. So far, a number of one-, two- and three-dimensional coordination frameworks, including helicates, honeycomb, square or rectangular grid, ladder, brick wall, and other uncommon frameworks,²⁻¹¹ have already been generated with linear or non-linear organic spacers. Self-assembly is currently the most efficient approach toward the design of coordination polymers of potential utility in fields such as nonlinear optics,¹² molecular magnetic materials¹³ and molecular recognition.¹⁴

To date, such polymers have been synthesized mostly by employing rigid ligands through coordination covalent bonding, supramolecular hydrogen bonding and π - π interactions.¹⁵⁻¹⁸ In contrast, flexible ligands have been seldom employed,¹⁹ and no such polymer materials that contain flexible diester-bridged pyridine-based ligands have been reported yet. Herein we report the syntheses of four new one-dimensional coordination polymers [$\text{Co}(\text{NCS})_2(\text{La})_2$]_n (1), [$\text{Co}(\text{NCS})_2(\text{La})_2 \cdot 2\text{THF}$]_n (2), [$\text{Co}(\text{NCS})_2(\text{Lb})_2 \cdot 0.5\text{MeOH}$]_n (3), and [$\text{Co}(\text{NCS})_2(\text{Lc})_2 \cdot 2\text{H}_2\text{O}$]_n (4) which contain such flexible ligands, obtained by reactions of $\text{Co}(\text{NCS})_2$ with $\text{pyCO}_2-(\text{CH}_2)_m-\text{O}_2\text{Cpy}$ (La: py = 4-pyridyl, $m = 2$; Lb: py = 4-pyridyl, $m = 3$; Lc: py = 4-pyridyl, $m = 4$) in appropriate solvents. The structures of these polymers have been characterized by elemental analysis, IR spectroscopy and thermogravimetry, and particularly by single-crystal X-ray

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diffraction techniques.

Crystal structures

Results and discussion

Syntheses

The four new coordination polymers 1–4 can be synthesized by self-assembly reactions of $\text{Co}(\text{NCS})_2$ (generated *in situ* from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and KNCS) with respective ligands La, Lb and Lc in appropriate solvent systems. It is worth noting that the crystals of 1–4 suitable for X-ray diffraction analysis were obtained by two ways: for 1 the single crystal was grown in a refrigerator at about 4 °C by slow evaporation of its mixed $\text{H}_2\text{O}/\text{MeOH}$ solvents, whereas for 2–4 those were grown during their preparation by slow diffusion of the two phases containing corresponding reactants. It is also worth noting that while red crystals of 1 were formed from $\text{Co}(\text{NCS})_2$ and La by adding KPF_6 in a $\text{MeOH}/\text{H}_2\text{O}$ solvent system, 2 was generated in a THF/MeCN solvent system. If KPF_6 was not added, 1 could not be produced. However, up to now we do not know what function KPF_6 has played in the formation of polymer 1.

The structure of 1 was characterized by single-crystal X-ray diffraction techniques. Fig. 1 shows the local coordination of the cobalt center, whereas Fig. 2 shows the extended structure and crystal packing of 1. Interestingly, polymer 1 contains two different one-dimensional chains. Fig. 1 shows the two segments, *i. e.*, segment a and segment b, in the two different chains. In these two segments Co is in a compressed octahedral environment with four long Co–N (pyridine rings) bonds [in segment a: Co(1)–N(11) 0.2174(8) nm, Co(1)–N(12) 0.2176(9) nm; in segment b: Co(2)–N(13) 0.2186(9) nm, Co(2)–N(14) 0.2209(9) nm] and two short Co–N (NCS) bonds [in segment a: Co(1)–N(1) 0.2062(11) nm; in segment b: Co(2)–N(2) 0.2022(10) nm]. The NCS ligands are almost linear with one N–C–S angle of 176.4(12)° in segment a and 176.5(10)° in segment b. Although the local coordination of the cobalt center is similar, the corresponding interatomic distances in segment a and in segment b are somewhat different. For example, Co(1)–N(12) [0.2176(9) nm] and C(1)–N(1) [0.1118(10) nm] in segment a are shorter than

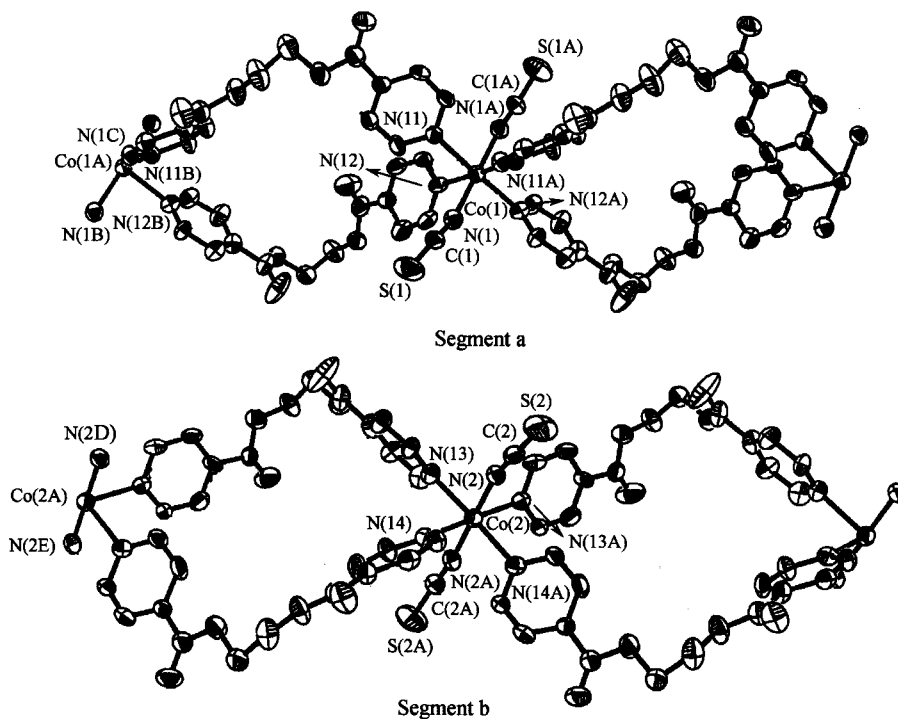


Fig. 1 ORTEP drawing of the local coordination of Co in 1 with thermal ellipsoids at the 50% probability, which includes segment a and segment b. The hydrogen atoms are omitted for clarity.

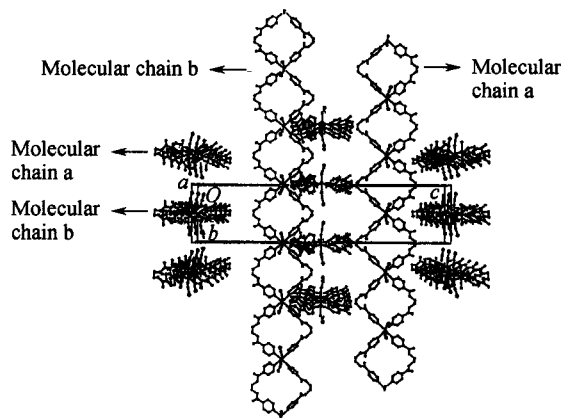


Fig. 2 Crystal packing of 1.

Co(2)—N(14) [0.2209(9) nm] and C(2)—N(2) [0.1145(10) nm] in segment b, whereas Co(1)—N(1) [0.2062(11) nm] in segment a is longer than Co(2)—N(2) [0.2022(10) nm] in segment b. The distances of two adjacent Co centers in the same molecular chain are all 1.2513 nm. Interestingly, Fig. 2 shows that the molecular chains a and b (along the crystallographic *a*-axis) are parallel and alternate to make a molecular layer and the molecular chains a and b (along the crystallographic *b*-axis) are also arranged parallel to each other and alternately to form another molecular layer. This type of structure with two adjacent layers stacked perpendicularly is completely different from Cd(NO₃)₂ [1,2-bis(4-pyridyl) ethane]_{1.5}²⁰ and to the best of our knowledge, this type of crystal packing in 1 is unprecedented.

The structure of 2 is similar to that of 1, whose local coordination environment around cobalt center is shown in Fig. 3. The Co atom is in a compressed octahedral environment with four long Co—N (pyridine rings) bonds [Co(1)—N(2B) 0.2197(4) nm and Co(1)—N(1) 0.2244(4) nm] and two short Co—N (NCS) bonds [Co(1)—N(3) 0.2044(4) nm]. The terminal NCS groups are linear with a bond angle of N(3)—C(15)—S(1) [179.1(5)°]. It is worthy noting that, in contrast to 1, polymer 2 only contains one type of one-dimensional molecular chain along *a* + *b* vector. In this polymeric chain there are a series of thirty-membered macrocyclic rings, which are formed by two adjacent Co ions and bridged La ligands. The distances of two adjacent Co ions in the same molecular chain are all 1.2775 nm. The shortest distance of two Co centers in the neighboring molecular chains along *a* + *b* vector is 0.9027 nm. Fig. 4 indicates the crystal packing of 2. The solvent

molecules (in this case, THF) occupy the voids among the neighboring molecular chains rather than be coordinated directly to the metal centers.

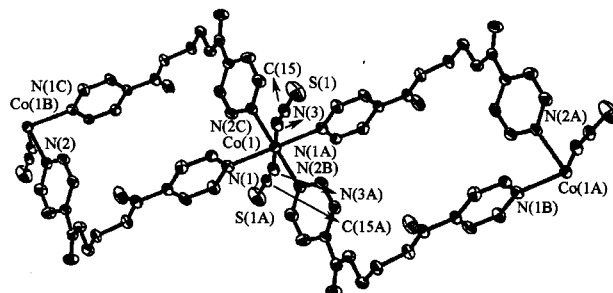


Fig. 3 ORTEP drawing of the local coordination of Co in 2 with thermal ellipsoids at the 50% probability. The hydrogen atoms are omitted for clarity.

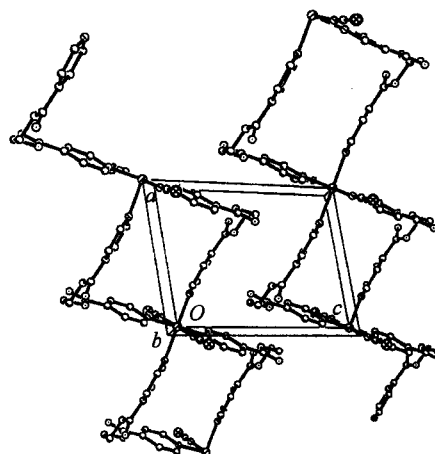


Fig. 4 Crystal packing of 2.

The structure of 3 is similar to that of 1 or 2. Fig. 5 shows the local coordination of the cobalt center in polymer 3. The Co atom is in a compressed octahedral environment with four long Co—N (pyridine rings) bonds [Co(1)—N(2) 0.2197(5) nm and Co(1)—N(3B) 0.2196(4) nm] and with two short Co—N (NCS) bonds [Co(1)—N(1) 0.2059(4) nm]. The NCS groups are almost linear with a bond angle of N(1)—C(1)—S(1) 178.0(6)°. The polymer contains a series of 32-membered rings, which are formed by two adjacent Co ions and two bridged Lb ligands. The distances of two adjacent Co centers in the same molecular chain are all 1.2973 nm. The shortest distance of two Co centers in the neighboring molecular chains along *c*-axis is 0.8393 nm. Fig. 6 indicates the crystal packing of 3. One-dimensional molecular chains view down crystallographic *c*-

axis. The MeOH solvent molecules occupy the voids among the neighboring molecular chains and there is no apparent interaction between the MeOH molecules and the host lattice in **3**.

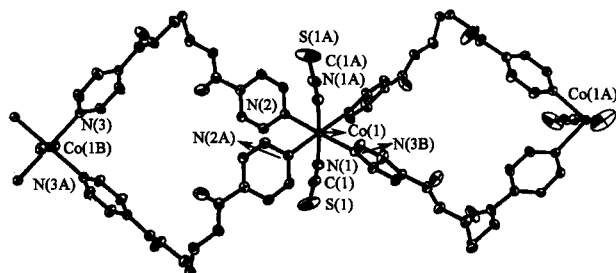


Fig. 5 ORTEP drawing of the local coordination of Co in **3** with thermal ellipsoids at the 50% probability. The hydrogen atoms are omitted for clarity.

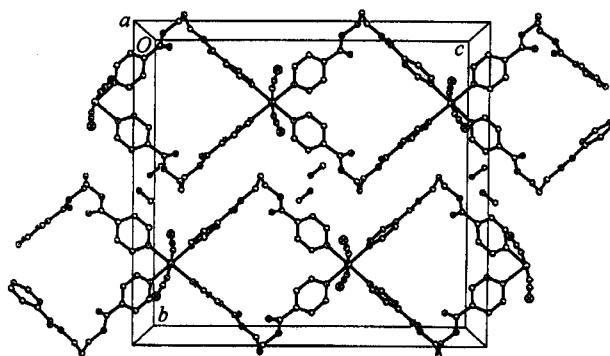


Fig. 6 Crystal packing of **3**.

The structure of **4** is similar to that of **1**, **2** or **3**. **Fig. 7** shows the local coordination of the cobalt center. The Co atom is in a compressed octahedral environment with four long Co—N (pyridine rings) bonds [Co(1)—N(1) 0.2210(3) nm and Co(1)—N(2) 0.2201(3) nm] and two short Co—N (NCS) bonds [Co(1)—N(3) 0.2061(4) nm]. The NCS groups are nearly linear with one N—C—S angle of 178.5(4)°. The connection between Co atoms and NCS groups is bent with a C(17)—N(3)—Co(1) angle [155.4(4)°] in **4**. This angle is close to that in Co(NCS)₂(pyz)₂ (pyz = pyrazine) [158.8°]²¹ and smaller than those of **1—3** [167.8(10)° in segment a of **1**, 168.7(9)° in segment b of **1**, 166.8(4)° in **2**, 172.8(5)° in **3**], which may result in more effective packing of the neighboring molecular chains in **4**. Similar to **2** and **3**, polymer **4** contains only one type of one-dimensional molecular chain consisting of a series of 34-

membered macrocyclic rings formed by two adjacent Co ions and two bridged Lc ligands. The distance of two adjacent Co in the same molecular chain are all 1.4475 nm. The shortest distance of two Co in the neighboring molecular chains along *a*-axis is 0.9184 nm. **Fig. 8** indicates the crystal packing of **4**. Its one-dimensional molecular chains run along crystallographic *a*-axis. The two disordered water molecules lie in 34-membered rings, which is quite different from the solvent molecules in **2** and **3** occupying the voids among the neighboring molecular chains. So, this makes **4** more effectively pack its neighboring molecular chains. It is worth pointing out that in contrast to **1—3**, polymer **4** has the pyridine rings and carboxylate groups in one molecular chain, which are overlapped with the pyridine rings and carboxylate groups in the neighboring molecular chains. The formation of this interesting structure is probably due to the flexible bidentate Lc ligand having a suitable length and the disordered water molecules lying in the macrocyclic rings.

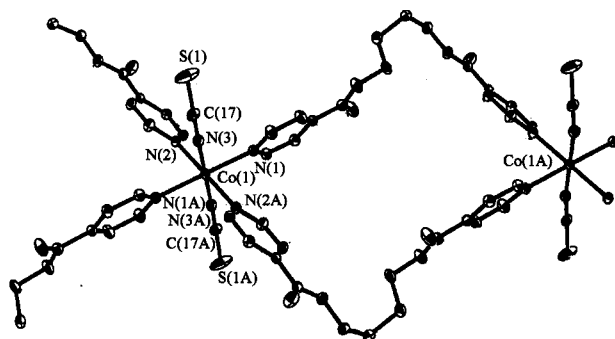


Fig. 7 ORTEP drawing of the local coordination of Co in **4** with thermal ellipsoids at the 50% probability. The hydrogen atoms are omitted for clarity.

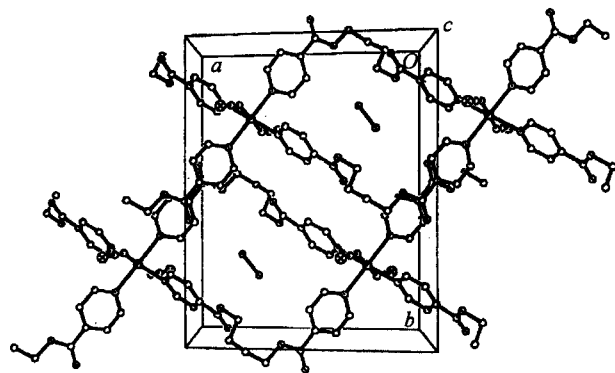


Fig. 8 Crystal packing of **4**.

Thermogravimetric analysis (TGA)

Polymers **1**–**4** were heated in a nitrogen atmosphere from 20 to 600 °C at a rate of 10 °C/min. For **1**, Thermogravimetric analysis (TGA) showed that a weight loss of 39.58%, occurring from 280 to 330 °C, corresponded to the loss of one La ligand per formula unit (calculated 37.83%). A further ill-defined weight loss was observed above 331 °C. TGA of **2** showed that the first weight loss of 16.46% was observed between 94–130 °C, corresponding to the loss of two THF molecules per formula unit (calculated 16.70%). A second weight loss of 31.04% was observed from 131 to 280 °C, corresponding to the loss of La ligand molecules (calculated 31.52%). A further ill-defined weight loss was observed from 280 to 600 °C. From the thermal decomposition behaviors of **1** and **2**, the temperature of the ligand weight loss was quite different in different coordination polymers assembled from the same ligand and the same transition metal ion. So, the decomposition mechanism was quite different. For **3**, TGA showed a weight loss of 1.81%, corresponding to the loss of 0.5 MeOH per formula unit (calculated 2.09%) in the temperature range of 56–140 °C. A second weight loss of 72.13% was observed from 141 to 600 °C, corresponding to the loss of Lb ligand per formula unit (calculated 74.98%). In contrast to **1**–**3**, TGA of **4** showed a weight loss of 2.13% from 95 to 135 °C, corresponding to the loss of one water molecule per formula unit (calculated 2.21%). A significant mass loss of 39.03% from 136 to 292 °C corresponded to the loss of one water molecule and one Lc ligand molecule (calculated 39.21%). A further ill-defined weight loss was observed between 290 and 600 °C. For **1**–**4**, the final residue was black and amorphous. From the four TGA, the losing temperature of the ligands of **2**–**4** was similar, but it was quite different for **1**. So, the structures of **2**–**4** were quite different from the structure of **1**. Single-crystal X-ray diffraction analysis also proved the views.

Experimental

Flexible diester ligands La, Lb and Lc were prepared according to the reported method.²² Reagents used in preparation of polymers **1**–**4** were commercially available and used without further purification, whereas solvents MeOH, MeCN, THF and H₂O were redistilled be-

fore use. Elemental analyses were made on an Elementar Vario EL elemental analyzer. IR spectra were recorded on a Bruker Vector 22 spectrophotometer in the 4000–400 cm⁻¹ range. Thermogravimetric analyses were carried out using the NETZSCH TG 209 instrument.

Synthesis of [Co(NCS)₂(La)₂]_n (**1**)

A solution of Co(NO₃)₂·6H₂O (20 mg, 0.07 mmol) and KNCS (14 mg, 0.14 mmol) in H₂O (3 mL) was stirred at room temperature for 0.5 h to give a light red solution containing Co(NCS)₂. To this solution were added KPF₆ (26 mg, 0.14 mmol) and a solution of La (38 mg, 0.14 mmol) in MeOH (8 mL). The mixture was stirred for 24 h at room temperature and then was filtered to give a precipitate. The precipitate was washed thoroughly with MeOH and then was dried under vacuum to give **1** (46.5 mg, 92.3% based on La) as a light yellow solid. IR (film) ν : 3437 (m), 3065 (w), 2907 (w), 2105 (s), 1732 (s), 1613(w), 1561 (w), 1482 (w), 1411 (m), 1343 (m), 1268 (s), 1220 (w), 1133 (m), 1062 (w), 1014 (w), 979 (w), 860 (w), 761 (m), 697 (m) cm⁻¹. Anal. calcd for C₃₀H₂₄CoN₆O₈S₂: C 50.07, H 3.36, N 11.68; found C 49.88, H 3.29, N 11.83. This light-yellow solid was suspended in H₂O (3 mL) and MeOH (8 mL) and the suspension was vigorously stirred for 48 h, which was filtered to give a filtrate. The filtrate was allowed to slow evaporation in a refrigerator at about 4 °C for two weeks to give reddish crystals of **1** suitable for single-crystal X-ray diffraction analysis.

Synthesis of [Co(NCS)₂(La)₂·2THF]_n (**2**)

A solution of Co(NO₃)₂·6H₂O (20 mg, 0.07 mmol) and KNCS (14 mg, 0.14 mmol) in MeCN (5 mL) was stirred at room temperature for 2 h to give a blue solution containing Co(NCS)₂. The solution was allowed to diffuse into a THF (5 mL) solution of La (38 mg, 0.14 mmol) at this temperature. After two weeks, **2** (58 mg, 96.0% based on La) was obtained as red crystals suitable for X-ray diffraction. IR (film) ν : 3445 (w), 3057 (w), 2970 (m), 2874 (m), 2066 (vs), 1736 (vs), 1617 (m), 1561 (m), 1494 (w), 1450 (m), 1415 (s), 1367 (m), 1323 (s), 1292 (s), 1264 (s), 1224 (m), 1129 (s), 1054 (s), 1038 (m), 1006 (m), 903 (m), 856 (m), 761 (s), 705 (s) cm⁻¹.

Anal. calcd for $C_{38}H_{40}CoN_6O_{10}S_2$: C 52.84, H 4.67, N 9.73; found C 52.77, H 4.70, N 9.51.

Synthesis of $[Co(NCS)_2(Lb)_2 \cdot 0.5CH_3OH]_n$ (**3**)

The blue MeCN solution containing $Co(NCS)_2$ prepared by the same procedure as described for **2**, was allowed to diffuse into a solution of Lb (40 mg, 0.14 mmol) in MeOH (5 mL) at room temperature for one week. Large red crystals of **3** suitable for X-ray diffraction were formed (52.7 mg, 98.5% based on Lb). IR (film) ν : 3441 (m), 3058 (w), 2968 (w), 2906 (w), 2064 (vs), 1732 (vs), 1613 (m), 1561 (m), 1499 (w), 1465 (m), 1415 (s), 1365 (w), 1327 (s), 1278 (vs), 1227 (m), 1136 (s), 1061 (m), 1016 (m), 933 (w), 856 (w), 761 (m), 702 (m), 689 (m) cm^{-1} . Anal. calcd for $C_{32.5}H_{30}CoN_6O_{8.5}S_2$: C 51.11, H 3.96, N 11.00; found C 51.01, H 4.10, N 10.90.

Synthesis of $[Co(NCS)_2(Lc)_2 \cdot 2H_2O]_n$ (**4**)

The light red aqueous solution containing $Co(NCS)_2$ prepared by the same procedure as described for **1** was allowed to diffuse into a solution of Lc (42 mg, 0.14 mmol) in EtOH (10 mL) at room temperature. After three weeks, red crystals of **4** suitable for X-ray diffraction analysis were obtained (54 mg, 95.0% based on Lc). IR (KBr) ν : 3572 (w), 3469 (m), 2970 (m), 2938 (w), 2066 (vs), 1732 (vs), 1613 (m), 1565 (m), 1462 (m), 1411 (s), 1383 (m), 1363 (m), 1327 (s), 1280 (vs), 1232 (s), 1216 (m), 1121 (s), 1058 (s), 1010 (m), 975 (m), 931 (m), 911

(w), 860 (m), 757 (s), 705 (s), 685 (s), 662 (w) cm^{-1} . Anal. calcd for $C_{34}H_{36}CoN_6O_{10}S_2$: C 50.31, H 4.47, N 10.35; found C 50.46, H 4.31, N 10.15.

X-Ray structure determination

Each of the single-crystals of **1**–**4** (**1**: 0.10 mm \times 0.20 mm \times 0.20 mm; **2**: 0.25 mm \times 0.20 mm \times 0.20 mm; **3**: 0.20 mm \times 0.25 mm \times 0.25 mm; **4**: 0.40 mm \times 0.30 mm \times 0.25 mm) was glued to a glass fiber and mounted on a Bruker SMART 1000 automated diffractometer, respectively. Data were collected, using Mo K α graphite-monochromated radiation ($\lambda = 0.071073$ nm) in the ω - 2θ scanning mode. Absorption corrections were performed using SADABS. The structures were solved by direct methods using the SHELXTL-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on F^2 . Hydrogen atoms were located by using the geometric method. The weighting scheme $W = 1/[s^2 \cdot (F_o^2) + (0.0600 P)^2 + 0.00 P]$ [where $P = (F_o^2 + 2F_c^2)/3$] was applied to the data for **1** {**2**: $W = 1/[s^2 \cdot (F_o^2) + (0.0319 P)^2 + 0.00 P]$, where $P = (F_o^2 + 2F_c^2)/3$; **3**: $W = 1/[s^2(F_o^2) + (0.0900 P)^2 + 0.00 P]$, where $P = (F_o^2 + 2F_c^2)/3$; **4**: $W = 1/[s^2(F_o^2) + (0.0852 P)^2 + 0.00 P]$, where $P = (F_o^2 + 2F_c^2)/3$ }. Selected bond lengths and bond angles are collected in Table 1. Crystal data and structure refinements are listed in Table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (E-mail: deposit@ccdc.cam.ac.uk) as supplementary publication, deposition code are 170389 for **1**, 170390 for **2**, 170391 for **3** and 170392 for **4**.

Table 1 Selected bond lengths (10^{-1} nm) and bond angles ($^\circ$) for **1**–**4**

Co(NCS) ₂ (La) ₂ (1)			
Co(1)—N(11)	2.174(8)	Co(1)—N(12)	2.176(9)
Co(1)—N(1)	2.062(11)	C(1)—N(1)	1.118(10)
S(1)—C(1)	1.609(13)	Co(2)—N(13)	2.186(9)
Co(2)—N(14)	2.209(9)	Co(2)—N(2)	2.022(10)
C(2)—N(2)	1.145(10)	S(2)—C(2)	1.617(14)
N(11)—Co(1)—N(12)	90.5(3)	N(11)—Co(1)—N(11A)	87.3(4)
N(12)—Co(1)—N(12A)	91.7(5)	C(1)—N(1)—Co(1)	167.8(10)
N(1)—Co(1)—N(1A)	179.5(4)	N(1)—Co(1)—N(11)	90.4(3)
N(1)—Co(1)—N(11A)	89.2(3)	N(1)—C(1)—S(1)	176.4(12)
N(13)—Co(2)—N(14)	90.8(3)	N(13)—Co(2)—N(13A)	91.9(5)

Continued

N(14)-Co(2)-N(14A)	86.5(5)	C(2)-N(2)-Co(2)	168.7(9)
N(2)-Co(2)-N(2A)	179.4(5)	N(2)-Co(2)-N(13)	90.7(4)
N(2)-Co(2)-N(13A)	89.8(4)	N(2)-C(2)-S(2)	176.5(10)
Co(NCS)₂(La)₂·2THF (2)			
Co(1)—N(1)	2.244(4)	Co(1)—N(2C)	2.197(4)
Co(1)—N(3)	2.044(4)	C(15)—N(3)	1.154(5)
S(1)—C(15)	1.602(5)	C(1)—N(1)	1.334(6)
N(1)-Co(1)-N(2C)	87.57(15)	N(1)-Co(1)-N(2B)	92.43(15)
C(15)-N(3)-Co(1)	166.8(4)	N(3)-Co(1)-N(3A)	180.000(1)
N(3)-Co(1)-N(1)	90.84(15)	N(3)-Co(1)-N(2C)	90.30(16)
N(3)-C(15)-S(1)	179.1(5)	N(2)-C(12)-C(11)	124.3(5)
Co(NCS)₂(Lb)₂·0.5CH₃OH (3)			
Co(1)—N(2)	2.197(5)	Co(1)—N(3B)	2.196(4)
Co(1)—N(1)	2.059(4)	C(1)—N(1)	1.130(6)
S(1)—C(1)	1.625(6)	C(11)—N(2)	1.344(7)
N(2)-Co(1)-N(2A)	88.1(2)	N(2)-Co(1)-N(3C)	91.04(16)
N(3B)-Co(1)-N(3C)	89.9(2)	C(1)-N(1)-Co(1)	172.8(5)
N(1)-Co(1)-N(1A)	176.9(3)	N(1)-Co(1)-N(2)	89.88(17)
N(1)-Co(1)-N(2A)	87.90(17)	N(1)-C(1)-S(1)	178.0(6)
Co(NCS)₂(Lc)₂·2H₂O (4)			
Co(1)—N(1)	2.210(3)	Co(1)—N(2)	2.201(3)
Co(1)—N(3)	2.061(4)	C(17)—N(3)	1.140(5)
S(1)—C(17)	1.609(5)	C(1)—N(1)	1.327(5)
N(1)-Co(1)-N(2A)	86.02(12)	N(1)-Co(1)-N(2)	93.98(12)
C(17)-N(3)-Co(1)	155.4(4)	N(3)-Co(1)-N(3A)	180.0(2)
N(3)-Co(1)-N(1)	90.86(13)	N(3)-Co(1)-N(2)	89.39(13)
N(3)-C(17)-S(1)	178.5(4)	C(1)-N(1)-C(5)	116.9(4)

Table 2 Crystal data and structure refinements for 1—4

Complex	1	2	3	4
Formula	Co(NCS) ₂ (La) ₂	Co(NCS) ₂ (La) ₂ ·2THF	Co(NCS) ₂ (Lb) ₂ ·0.5CH ₃ OH	Co(NCS) ₂ (Lc) ₂ ·2H ₂ O
Formula weight	719.60	863.81	763.67	811.74
Crystal system	Tetragonal	Triclinic	Orthorhombic	Monoclinic
Space group	I4(1)	P-1	Ibca	C2/c
a (nm)	1.2513(3)	0.9027(2)	1.2453(3)	1.4475(5)
b (nm)	1.2513(3)	1.1378(3)	2.4020(5)	1.7775(6)
c (nm)	5.5192(19)	1.1563(3)	2.5950(5)	1.5709(5)
α (°)	90	114.914(5)	90	90
β (°)	90	94.303(5)	90	105.161(60)
γ (°)	90	103.437(5)	90	90
V (nm ³)	8.641(4)	1.0273(5)	7.762(3)	3.901(2)
Z	8	1	8	4
D (calcd) (g/cm ³)	1.106	1.396	1.307	1.382
μ (mm ⁻¹)	0.538	0.582	0.604	0.608

Continued

Complex	1	2	3	4
<i>T</i> (K)	293(2)	293(2)	293(2)	298(2)
Reflections collected	17668	4322	7151	8021
Independent reflections	7009	3621	2854	3457
Data/restraints/parameters	7009/1/425	3621/3/259	2854/0/228	3457/0/241
Goodness-of-fit on F^2	0.915	1.003	1.030	0.960
<i>R</i>	0.0668	0.0634	0.0643	0.0549
<i>R_w</i>	0.1252	0/1070	0.1472	0.1362
Largest diff. peak and hole (e/nm ³)	318 and -187	421 and -320	516 and -396	700 and -698

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