Coordination networks assembled from Co(NCS)$_2$ and 4’-[4-(naphthalen-1-y1)phenyl]-3,2′:6′,3′′-terpyridine: Role of lattice solvents

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**Abstract**

The preparation and characterization of 4’-[4-(naphthalen-1-yl)phenyl]-3,2′:6′,3′′-terpyridine (1) are described. Reactions of 1 with Co(NCS)$_2$ under conditions of crystal growth by layering using different solvent combinations produced crystals of [Co(1)$_2$(NCS)$_2$]$_n$ 2nCHCl$_3$ and [Co(1)$_2$(NCS)$_2$]$_n$ 2nC$_6$H$_5$Me, each of which comprised a (4,4) net. The orientations of 1 with respect to the planar network defined by the Co atoms are significantly different in [Co(1)$_2$(NCS)$_2$]$_n$ 2nC$_6$H$_5$Me compared to [Co(1)$_2$(NCS)$_2$]$_n$ 2nCHCl$_3$, and the toluene molecules in [Co(1)$_2$(NCS)$_2$]$_n$ 2nC$_6$H$_5$Me are involved in π-stacking interactions. The solvent-accessible void-space in the latter consists of a series of linked cavities in contrast to the open channels in [Co(1)$_2$(NCS)$_2$]$_n$ 2nCHCl$_3$. Thermogravimetric analysis was used to investigate solvent loss and uptake in the two coordination networks. After solvent loss from [Co(1)$_2$(NCS)$_2$]$_n$ 2nCHCl$_3$, CHCl$_3$, CDCl$_3$, or C$_2$H$_2$Cl$_2$ could be taken up by the lattice. In contrast, removal of toluene from [Co(1)$_2$(NCS)$_2$]$_n$ 2nC$_6$H$_5$Me was found to be irreversible.

**Keywords:**
3,2′:6′,3′-Terpyridine
Cobalt
Lattice solvent
Coordination networks

1. Introduction

While less well developed than that of 2,2′:6′,2′-terpyridine (tpy) [1–5], the coordination chemistry of 3,2′:6′,3′-terpyridine (3,2′:6′,3′-tpy) has gained increased attention over the last decade, especially in the context of coordination polymers and networks [6–9]. The 3,2′:6′,3′-tpy metal-binding domain is conformationally flexible, and Scheme 1 displays its three limiting, planar conformations. Different conformations can be observed in the solid-state structures of 3,2′:6′,3′-tpy ligands depending upon the 4′-substituents, both in the free ligands [10] and in coordination polymers [11–13]. Conformations A and B (Scheme 1) can be classified as divergent and are to be the expected limiting conformations favoured when 3,2′:6′,3′-tpy ligands are incorporated as linkers in coordination polymers. In contrast, conformation C can participate in the assembly of small discrete multinuclear complexes [12,14], in addition to coordination polymers. Note that the central pyridine ring remains uncoordinated in all cases.

Combinations of Co(NCS)$_2$ and 4'-functionalized 3,2′:6′,3′-tpy ligands typically lead to (4,4) networks with each Co(II) centre bound by trans-thiocyanato ligands and four pyridine N-donors of four different 3,2′:6′,3′-tpy ligands [10,15,16]. Similarly, reactions of Co(NCS)$_2$ and 4'-functionalized 4,2′:6′,4′-tpy ligands also usually produce 2-dimensional (4,4) nets [17–22], although the unexpected assembly of 3-dimensional architectures has been observed in a few cases [20,23]. Where crystals have been grown by layering MeOH solution of Co(NCS)$_2$ under ambient conditions, the dominant product may be a 1-dimensional polymer [Co(NCS)$_2$(MeOH)$_2$(L)]$_n$ (L = 4′-functionalized 3,2′:6′,3′-tpy or 4,2′:6′,4′-tpy) [15,19,21].

We have previously carried out systematic investigations of the effects of different 4′-substituents R on the assembly of [Co(NCS)$_2$(4′-R-3,2′:6′,3′-tpy)$_2$]$_n$ 2-dimensional nets [10,15,16], and have demonstrated a change between conformations A and B (Scheme 1) as a consequence of changing the 4′-substituent. Motivated by these results and the observation that many of the 2D structures contain lattice solvent molecules, we decided to focus on a single 3,2′:6′,3′-tpy ligand (1, Scheme 2) and explore the effects of using different pairs of solvents in crystal growth experiments. Here we report the coordination networks assembled when MeOH or MeCN solutions of Co(NCS)$_2$ were layered...
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2.2. Compound 1

4-(Naphthalen-1-yl)benzaldehyde (1.00 g, 4.31 mmol) was dissolved in EtOH (50 mL) and then 3-acetylpyridine (1.04 g, 9.85 mmol, 8.62 mmol) and crushed KOH (0.484 g, 8.62 mmol) were added to the solution. An excess of aqueous NH$_3$ (32%, 16.6 mL) was slowly added to the reaction mixture which was then stirred at room temperature overnight. The solid that formed was collected by filtration, washed with H$_2$O (3 × 10 mL) and EtOH (3 × 10 mL), recrystallized from EtOH and dried in vacuo. Compound 1 was isolated as a colorless solid (0.789 g, 81% yield). M.p. = 225 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ ppm 9.46 (dd, $J = 2.3$, 0.9 Hz, 2H, H$^D$), 8.75 (dd, $J = 4.9$, 1.6 Hz, 2H, H$^D$), 8.68 (dt, $J = 8.0$, 2.0 Hz, 2H, H$^D$), 8.11 (s, 2H, H$^D$), 7.94 (overlapping m, 5H, H$^B$), 7.72 (m, 2H, H$^C$), 7.62–7.47 (overlapping m, 6H, H$^A$), $^{13}$C NMR chemical shifts were referenced with respect to residual solvent peaks ($\delta$ TMS = 0). A Shimadzu LCMS-2020 instrument was used to record electrospray ionization (ESI) mass spectra, and FT-infrared (IR) spectra were recorded on a PerkinElmer UATR Two instrument. A Shimadzu UV-2600 spectrophotometer was used to record solution absorption spectra.

A solution of Co(NCS)$_2$ (5.3 mg, 0.030 mmol) in MeCN (6 mL) was layered over a CHCl$_3$ solution (5 mL) of 1 (13.1 mg, 0.030 mmol). Pink block-like crystals grew after 10 days. A single crystal was selected for X-ray diffraction and the remaining crystals were washed with MeCN and CHCl$_3$, dried under vacuum and analysed by PXRD and FT-IR spectroscopy.

2.3. [Co(1)$_2$(NCS)$_3$]$_n$·2nCHCl$_3$

A solution of Co(NCS)$_2$ (5.3 mg, 0.030 mmol) in MeCN (6 mL) was layered over a toluene solution (6 mL) of 1 (13.1 mg, 0.030 mmol). Pink plate-like crystals grew after 7 days. A single crystal was selected for X-ray diffraction and the remaining crystals were washed with MeOH and toluene, dried under vacuum and analysed by PXRD and FT-IR spectroscopy.

2.5. Crystallography

Single crystal data were collected on a Bruker APEX-II diffractometer (CuK$\alpha$ radiation) with data reduction, solution and refinement using the programs APEX [26], ShelXT [27], Olex2 [28] and ShelXL v. 2014/7 [29]. All H atoms were included at geometrically calculated positions and refined using a riding model with Uiso ($\alpha$) = 1.2 of the parent atom. Structure analysis and structural diagrams used CSD Mercury 2020.1 [30]. In [Co(1)$_2$(NCS)$_3$]$_n$·2nCHCl$_3$, each toluene solvent molecule was disordered over a symmetry element, with site occupancies of 50%; the toluene molecules were refined isotropically. In [Co(1)$_2$(NCS)$_3$]$_n$·2nCHCl$_3$, the solvent area was treated using a solvent mask, and the electron density removed corresponded to 2 molecules of CHCl$_3$ per Co atom; this was added to the formulae and appropriate numbers.

PXRD patterns were collected at ca. 298 K in transmission mode.
using a Stoe Stadi P diffractometer with Cu Kα1 radiation (Ge(111) monochromator) and a Dectris Mythen 1 K detector. Whole-pattern decomposition (profile matching) analysis [31–33] of the diffraction patterns was performed with the package FullProf Suite [33,34] (v. September 2020) using a previously determined instrument resolution function based on a NIST640d standard. The structural models were taken from the single crystal X-Ray diffraction refinements. Refined parameters in Rietveld were: scale factor, zero shift, lattice parameters, Co and S atomic positions, background points and peaks shapes as a Thompson-Cox-Hastings pseudo-Voigt function. Preferred orientations were included in the analysis as a March-Dollase multi-axial phenomenological model.

2.6. \( \text{[Co(1)₂(NCS)]₂}_n \cdot 2n\text{CHCl}_3 \)

\( \text{Cd}_6\text{H}_4\text{Cl}_4\text{CoN}_6\text{S}_2 \), \( M_r = 1284.919 \), pink block, monoclinic, space group \( P2_1/n, a = 10.9048(6), b = 18.5289(10), c = 15.4837(8) \), \( \beta = 91.214(3) \), \( V = 3127.8(3) \), \( D_e = 1.364 \text{ g cm}^{-3} \), \( T = 150 \), \( Z = 2 \), \( \mu(\text{CuKα}) = 5.508 \text{ mm}^{-1} \). Total 18,857 reflections, 5644 unique (\( R_{int} = 0.0327 \)). Refinement of 5210 reflections (340 parameters) with \( I > 2\sigma(I) \) converged at final \( R_I = 0.0442 \) (all data = 0.0474), \( wR_2 = 0.1226 \) (\( wR_2 \) all data = 0.1261), gof = 1.0431. CCDC 2087183.

2.7. \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{C}_6\text{H}_5\text{Me} \)

\( \text{Cd}_6\text{H}_8\text{CoN}_6\text{S}_2 \), \( M_r = 1230.37 \), pink plate, monoclinic, space group \( P2_1_2_1/\alpha, a = 14.6063(5), b = 11.8567(5), c = 18.3485(6) \), \( \beta = 92.912 \) (2), \( V = 3173.5(2) \), \( D_e = 1.288 \text{ g cm}^{-3} \), \( T = 150 \), \( Z = 2 \), \( \mu(\text{CuKα}) = 3.137 \text{ mm}^{-1} \). Total 20,072 reflections, 5706 unique (\( R_I = 0.0368 \)). Refinement of 5130 reflections (375 parameters) with \( I > 2\sigma(I) \) converged at final \( R_I = 0.0583 \) (all data = 0.0646), \( wR_2 = 0.1557 \) (\( wR_2 \) all data = 0.1612), gof = 1.050. CCDC 2087184.

3. Results and discussion

3.1. Ligand synthesis and characterization

Compound 1 was prepared by the one-pot strategy of Wang and Hanan [35] by reaction of two equivalents of 3-acetylpyridine with 4-(naphthalen-1-yl)benzaldehyde under basic conditions and addition of aqueous NH₃. The ligand was isolated in 42.0% yield as a colorless solid, \( \text{H}_{18}\text{N}_{13}\text{C}_6\text{O}_2 \). The \( ^1\text{H} \) and \( ^{13}\text{C}(\text{H}) \) NMR spectra (Figs. S2 and S3, respectively) were assigned using NOESY, COSY, HMBC (Fig. S4) and HMBC (Fig. S5) spectra, and were in accord with the structure shown in Scheme 2. Overlap of the signals for the naphthyl protons made unambiguous assignment of these signals difficult. The IR spectrum is shown in Fig. S6, with diagnostic, strong bands in the fingerprint region at 796, 773 and 695 cm⁻¹. Fig. 1 displays the solution absorption spectrum of 1, and the absorption bands are assigned to π*→π transitions. The spectrum closely resembles that of 4’-(naphthalen-1-yl)phenyl-4,2’,6’,4’-terpyridine [36] which is an isomer of 1.

3.2. Coordination networks \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) and \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{C}_6\text{H}_5\text{Me} \)

Single crystals of \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) and \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{C}_6\text{H}_5\text{Me} \) were grown under ambient conditions by layering either a MeCN solution of Co(NCS)₂ over a CHCl₃ solution of 1, or a MeOH solution of Co(NCS)₂ over a toluene solution of 1, respectively. X-ray quality crystals were selected and the remaining crystals were used for PXRD analysis (see Section 3.3). The two compounds crystallize in the monoclinic space groups \( P2_1_1_2 \) and \( P2_1_2_1_1 \), respectively, and each possesses a 2D-network with the Co(II) centers acting as 4-connecting nodes. The structures of the asymmetric units with symmetry-generated atoms are shown in Fig. 2. The Co atom in each structure is six-coordinate and lies on an inversion center, being bonded to four different, but crystallographically equivalent, ligands 1. Selected bond lengths and angles in each cobalt(II) coordination sphere are given in Table 1 and are unexceptional.

In \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \), 1 adopts conformation A in Scheme 1, whereas in \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{C}_6\text{H}_5\text{Me} \), conformation B (Scheme 1) is observed. This results in distinct differences between the 2D-assemblies in \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) and \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{C}_6\text{H}_5\text{Me} \). This is quantified by a comparison of the angles between the planes of adjacent aromatic rings in the ligand in each structure presented in Table 2. When 1 adopts conformation A (Scheme 1), the vectorial properties of each N1 and N3 in each ligand are equivalent. In contrast, the different vectorial properties of the N-donor lone pairs when ligand 1 is in conformation B lead to three possible coordination modes for a trans-arrangement of ligands. In a previous publication, we defined the labels in and out to describe the orientation of each N lone pair with respect to the central pyridine ring (Scheme 3) [13]. Since the Co atom in \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) lies on a center of symmetry, only two of the three coordination modes shown in Scheme 3 are permitted. Since each Co in \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) is crystallographically equivalent, both \( \text{trans out}/\text{out} \) and \( \text{in}/\text{in} \) arrangements are present at each metal center (Fig. 3a). This contrasts with the arrangement in \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) in which all motifs are \( \text{out}/\text{out} \) (Fig. 3b), leading to a significant difference between the \( \text{[Co(1)₂(NCS)]}_2 \) units in the networks (Fig. 3a versus 3b).

Part of the (4,4) network in \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) is shown in Fig. 4a. The Co atoms are coplanar, and the (4-naphthalen-1-yl)phenyl substituents protrude above and below the plane defined by the Co atoms. Around each rhombus in the net, the 4-(naphthalen-1-yl)phenyl groups are arranged in an \( \text{up}/\text{up}/\text{down}/\text{down} \) configuration (Fig. 5g). The adjacent 2D-sheets are locked together by face-to-face π-stacking interactions between naphthalenyl rings in one layer with the central pyridine ring of the 3,2′:6′,3′-tpy units in the neighboring sheet (Fig. 4c). Metrics for the π-π interaction are centroid…centroid = 3.60 Å, and angle between the ring planes = 3.1°. The \( \text{up}/\text{up}/\text{down}/\text{down} \) configuration of the arene substituents leads to extended π-stacking interactions which interconnect all adjacent sheets in the lattice. Viewing the structure of \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) down the a-axis without solvent molecules present reveals approximately linear channels (Fig. 4d) and the solvent accessible void space in the lattice is ca. 25% of the total volume.

In \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{C}_6\text{H}_5\text{Me} \), each toluene molecule is disordered over a symmetry element, with 50% site occupancies of head-to-tail positions. For the discussion below, one position for each toluene molecule is considered. Two views of the (4,4) net in \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{C}_6\text{H}_5\text{Me} \) are depicted in Fig. 5a and 5b. As in \( \text{[Co(1)₂(NCS)]}_2 \cdot 2n\text{CHCl}_3 \) (Fig. 4), the Co atoms in each sheet are coplanar, and the terpyridines adopt an \( \text{up}/\text{up}/\text{down}/\text{down} \) arrangement around each rhombus (Fig. 5e). Inspection of Fig. 5a and 5c reveals that ligands 1 lie over the rhombuses in the net in

**Fig. 1.** The absorption spectrum of 1 (MeCN, \( 2.0 \times 10^{-5} \) mol dm\(^{-3}\)).
The structures of the asymmetric units with symmetry-generated atoms in (a) \([\text{Co}(\text{NCS})_2]_2\text{CHCl}_3\) (symmetry codes: i = –x, 1–y, 1–z; ii = 1/2–x, –1/2 + y, 1/2–z; iii = 1/2–x, 1/2 + y, 1/2–z; iv = 1/2–x, 1/2 + y, 1/2–z; v = –1/2 + x, 1/2–y, 1/2 + z), and (b) \([\text{Co}(\text{NCS})_2]_2\text{C}_6\text{H}_5\text{Me}\) (symmetry codes: i = 1–x, 1–y, 1–z; ii = –1/2 + x, 1/2–y, 1/2–z; iii = 1–x, 1–y, 1–z; iv = x, 1/2–y, 1/2–z; v = 1–x, –1/2 + y, 1/2–z). Ellipsoids are plotted at a 40% probability level, and H atoms and solvent molecules are omitted.

![Figure 2](image)

**Table 1**

Selected bond lengths and angles in \([\text{Co}(\text{NCS})_2]_2\text{CHCl}_3\) and \([\text{Co}(\text{NCS})_2]_2\text{C}_6\text{H}_5\text{Me}\).

| Compound | Co–N\(_{\text{NCS}}\)/Å | Co–N\(_{\text{py}}\)/Å | N\(_{\text{py}}\)–Co–N\(_{\text{NCS}}\)/° | N\(_{\text{py}}\)–Co–N\(_{\text{py}}\)/° |
|-----------|----------------|----------------|----------------|----------------|
| \([\text{Co}(\text{NCS})_2]_2\text{CHCl}_3\) | 2.076(9) | 2.188(6) | 90.30(6), 89.70(6), 92.25(6), 87.75(6) | 88.19(6), 91.81(6) |
| \([\text{Co}(\text{NCS})_2]_2\text{C}_6\text{H}_5\text{Me}\) | 2.084(2) | 2.190(2) | 88.26(9), 91.74(9), 87.97(9), 92.03(9) | 89.60(9), 90.40(9) |

**Table 2**

Angles between planes of adjacent aromatic rings in \([\text{Co}(\text{NCS})_2]_2\text{CHCl}_3\) and \([\text{Co}(\text{NCS})_2]_2\text{C}_6\text{H}_5\text{Me}\).

| Compound | \(\text{py}^{\text{N}}/\text{py}^{\text{NCS}}/°\) | \(\text{py}^{\text{N}}/\text{py}^{\text{NCS}}/°\) | \(\text{py}^{\text{N}}/\text{C}_6\text{H}_5/°\) | \(\text{C}_6\text{H}_5/\text{naphthyl}/°\) |
|-----------|----------------|----------------|----------------|----------------|
| \([\text{Co}(\text{NCS})_2]_2\text{CHCl}_3\) | 15.8 | 15.6 | 34.8 | 53.6 |
| \([\text{Co}(\text{NCS})_2]_2\text{C}_6\text{H}_5\text{Me}\) | 33.2 | 22.4 | 50.5 | 64.3 |

**Scheme 3.** Three coordination modes are possible for a trans-arrangement of ligands at a Co center, but only the left-hand two modes are permitted when the metal ion lies at a center-of-symmetry.

\([\text{Co}(\text{NCS})_2]_2\text{C}_6\text{H}_5\text{Me}\), in contrast to the upright positions found in \([\text{Co}(\text{NCS})_2]_2\text{CHCl}_3\) (Figs. 4a and S7). This impacts on the solvent accessible voids in the lattice (Fig. 5d and S8) which comprise a series of interlinked cavities (ca. 24% of the total lattice volume) in contrast to the open channels in \([\text{Co}(\text{NCS})_2]_2\text{CHCl}_3\). The toluene molecules occupying the cavities are involved in a face-to-face π-interaction with the pyridine ring containing N2, and C–H\(_{\text{py}}\)–π\(_{\text{toluene}}\) contacts involving the pyridine rings with N2 and N3 (Fig. S10). For the face-to-face contact, the distance between the ring centroids is 3.8 Å and the angle between the ring planes is 9.8°. For the C–H\(_{\text{py}}\)–π\(_{\text{toluene}}\) contacts, the H…centroid distances are 3.2 and 3.4 Å, and the C–H…centroid angles are 151 and 168°, respectively.

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Fig. 3. The arrangement of ligands 1 in the coordination sphere of the Co atom in (a) [Co(1)_2(NCS)_2]_n \cdot 2nC_6H_5Me, and (b) [Co(1)_2(NCS)_2]_n \cdot 2nCHCl_3. See Scheme 3 for definitions of the in and out labels.

Fig. 4. The structure of [Co(1)_2(NCS)_2]_n \cdot 2nCHCl_3: (a) Part of one (4,4) net with connection lines between the Co atoms to emphasize the network topology; H atoms and solvent molecules are omitted for clarity. (b) The network viewed from the side to illustrate the positions of the peripheral naphthalenyl groups. (c) Stacking of naphthalenyl and 3,2'-5',3''-domains in adjacent 2D-sheets. (d) View down the a-axis (solvent molecules omitted) showing the void (calculated using a contact surface map with probe radius = 1.2 Å); drawn using Mercury 2020.1 [30].
diffraction were representative of the bulk crystalline materials, we carried out PXRD on the remaining crystals in each crystallization tube. PXRD patterns (in red in Fig. 6) and the patterns predicted from the (see Sections 2.3 and 2.4). Fig. 6 shows comparisons of the experimental 3.3. Analysis of bulk samples of the single crystals

In order to verify that the crystals selected for single-crystal X-ray diffraction were representative of the bulk crystalline materials, we carried out PXRD on the remaining materials in each crystallization tube (see Sections 2.3 and 2.4). Fig. 6 shows comparisons of the experimental PXRD patterns (in red in Fig. 6) and the patterns predicted from the single crystal structures (in black in Fig. 6). For each compound, there was a match for every peak in the predicted pattern with those in the experimental PXRD pattern. No additional peaks were observed in the PXRD of the bulk materials.

The IR spectra of the cobalt(II) compounds are shown in Figs. S10 and S11. Bands in the fingerprint region are mainly characteristic of coordinated 1. The dominant absorption at 2063 cm$^{-1}$ for [Co(NCS)$_2$)$_2$·2nCHC$_3$ and 2070 cm$^{-1}$ for [Co(NCS)$_2$)$_2$·2nC$_6$H$_5$Me arises from the CN stretching mode of the thiocyanato ligands.

3.4. Thermogravimetric analysis: Solvent removal and re-entry

Crystals of [Co(NCS)$_2$)$_2$·2nCHCl$_3$ were heated to 80 °C in the TGA instrument, and this temperature was maintained for 10 min. Loss of CHCl$_3$ was detected (Fig. 7) with mass peaks at m/z 83.0, 85.0 and 87.0 corresponding to CHCl$_3$ as the dominant fragment [37]. After cooling, the sample retained crystallinity. The weight loss of 17.1% corresponded to the loss of approximately 2 CHCl$_3$ molecules per formula unit (calculated 18.6% from the molecular formula). In order to investigate whether the coordination network maintained its integrity, the same sample was placed in contact with CHCl$_3$ vapor for 48 h and was again analysed using TGA (Fig. S12). Loss of CHCl$_3$ was again detected confirming that, after the initial removal of solvent, the coordination assembly was able to re-absorb CHCl$_3$. A third cycle was performed with the same crystals exposed to CDCl$_3$ vapor for 24 h and then analysed by TGA (Fig. S13). Loss of CDCl$_3$ was confirmed by the presence of mass peaks at m/z 84.0, 86.0 and 88.0 corresponding to the CDCl$_3^+$ ion. In a fourth cycle, the crystalline material was recovered from the preceding TGA experiment and exposed to CH$_2$Cl$_2$ vapor for 24 h. The TGA trace of the resultant crystal showed loss of CH$_2$Cl$_2$ (m/z 49.0, 51.0, 84.0 and 86.0 arising from CH$_2$Cl$^+$ and CH$_3$Cl$_2^+$) at around 40 °C (Fig. S14). Finally, an analogous experiment was attempted using CCl$_4$ but the TGA of the crystals after exposure to CCl$_4$ vapor for 24 h revealed no change in mass over a period of 10 min heating at 80 °C. This is consistent with no uptake of CCl$_4$ into the crystal lattice.

[Co(NCS)$_2$)$_2$·2nC$_6$H$_5$Me was also analysed by TGA. It was first heated to 150 °C and this temperature was maintained for 30 min. The loss of toluene was detected with peaks in the mass spectrum of the TGA-MS at m/z 92.0, 91.0 (highest intensity peak), 65.0 and 39.0 (Fig. 8). The weight loss of 14.4% (Fig. 8) corresponded to complete loss of two molecules of toluene from the lattice (calculated 15.0%). The same sample was then placed in contact with toluene vapor for 24 h, and the subsequent TGA analysis showed no appreciable mass loss, consistent with the fact that once toluene had been removed from [Co(NCS)$_2$)$_2$·2nC$_6$H$_5$Me, it was unable to be re-absorbed. This is consistent with the presence of the aromatic solvent in [Co(NCS)$_2$)$_2$·2nC$_6$H$_5$Me playing a structural role in contrast to the CHCl$_3$ in [Co(NCS)$_2$)$_2$·2nCHCl$_3$ occupying channels in a non-ordered manner. The π-stacking interactions are key to the former, and we suggest that these may template the assembly of the network in [Co(NCS)$_2$)$_2$·2nC$_6$H$_5$Me and that there is a partial loss in crystallinity (confirmed with PXRD) once the solvent is removed.

4. Conclusions

We have reported the synthesis and characterization of compound 1 which contains a 3,2′-6′,3′′-tpy metal-binding domain. Under ambient conditions and using a solvent layering method, crystals of [Co(NCS)$_2$)$_2$·2nCHCl$_3$ and [Co(NCS)$_2$)$_2$·2nC$_6$H$_5$Me were obtained.
Single-crystal X-ray diffraction revealed that each is a 2D-coordination network with the Co atoms acting as 4-connecting nodes. In [Co(1)\textsubscript{2}(NCS)\textsubscript{2}]\textsubscript{2}2nCHCl\textsubscript{3}, the 3,2′:6′,3″-tpy unit in I adopts conformation A (Scheme 1) while conformation B is observed in [Co(1)\textsubscript{2}(NCS)\textsubscript{2}]\textsubscript{2}2nC\textsubscript{6}H\textsubscript{5}Me. PXRD was used to confirm that the single crystals were representative of the bulk materials. In [Co(1)\textsubscript{2}(NCS)\textsubscript{2}]\textsubscript{2}2nCHCl\textsubscript{3}, ligands I are directed above and below the planar (4,4) net defined by the Co atoms. This leads to open channels running perpendicular to the nets. In [Co(1)\textsubscript{2}(NCS)\textsubscript{2}]\textsubscript{2}2nC\textsubscript{6}H\textsubscript{5}Me the toluene molecules, are involved in π-stacking interactions, and the solvent-accessible void-space comprises interlinked cavities. By using TGA-MS, we demonstrated that, after initial solvent loss from [Co(1)\textsubscript{2}(NCS)\textsubscript{2}]\textsubscript{2}2nCHCl\textsubscript{3}, CHCl\textsubscript{3}, CDCl\textsubscript{3} or CH\textsubscript{2}Cl\textsubscript{2} could be sequentially introduced and removed from the same sample of single crystals. In stark contrast, the removal of toluene from [Co(1)\textsubscript{2}(NCS)\textsubscript{2}]\textsubscript{2}2nC\textsubscript{6}H\textsubscript{5}Me resulted in a partial loss in crystallinity (confirmed with PXRD), consistent with the aromatic solvent playing a role in stabilization of the structure.

**Author Contributions**

Experimental: D.R. and S.N.; Crystallography: A.P.; Powder diffraction and analysis: D.R.; Manuscript writing and structure analysis: D.R. and C.E.H.; Manuscript editing: all authors; Funding, project concepts and supervision: C.E.H. and E.C.C.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests that could have appeared to influence the work reported in this paper.

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**Appendix A. Supplementary data**

Supplementary data (Figs. S1–S6: Mass spectrum, NMR spectra and IR spectrum of 1. Figs. S7–S9: Additional crystallographic figures. Figs. S10 and S11: IR spectra of the coordination compounds. Figs. S12–S14: TGA-MS traces) to this article can be found online at https://doi.org/10.1016/j.poly.2021.115445.

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