

# Syntheses and crystal structures of cobalt(II) and nickel(II) complexes with thiocyanate and pyridyl carboxylic acid

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The syntheses and crystal structures of  $[\text{Co}(\mu\text{-NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$ ,  $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{isonicH})_2]\cdot(\text{isonicH})\cdot 2\text{H}_2\text{O}$  are reported, where nicH is nicotinic acid; isonicH is isonicotinic acid. In the crystals of the two complexes, (iso)nicotinic acids are not deprotonated and thus the carboxy groups act as both donors and acceptors of H-bonds to form networks.

**Keywords:** cobalt(II), nickel(II), thiocyanate, nicotinic acid, isonicotinic acid

Hydrogen-bonded coordination networks have been receiving much attention in recent years, as utilisation of the advantages of both hydrogen bonds and coordinative bonds represents an effective methodology in construction of supramolecular assemblies.<sup>1</sup> The preparation of coordination compounds with peripheral H-bonding substituents is a challenge for chemists who are interested in this type of network, since the common H-bond donors and acceptors themselves usually have strong coordinative ability and could coordinate to metals instead of forming hydrogen bonds. We have successfully prepared a coordination polymer –  $[\text{Cd}(\mu\text{-NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$  (nicH = nicotinic acid, hereafter); the nicotinic acids coordinate to the 1D chain of  $[\text{Cd}(\text{NCS})_2]_n$  through their pyridyl ends and the carboxyl groups are H-bonded to afford 2D network, where nicotinic acid is incorporated as the guest.<sup>2</sup> Sekiya recently reported a series of hydrogen-bonded coordination networks consisting of isonicotinic acid (isonicH) dimers and 1D chains of  $[\text{Ni}(\text{SCN})_2]_n$ , which can host neutral aromatic guests. In the above-mentioned cases, thiocyanato-anions balance the positive charges of metal ions, which might contribute to prevent the deprotonation of carboxy groups of (iso)nicotinic acids, and thus facilitate the formation of H-bonded dimers of carboxylic acids.<sup>3</sup> As a part of our ongoing research in construction of H-bonded supramolecular assemblies exploiting the pyridyl carboxylic acids, we report herewith the synthesis, characterisation and crystal structures of Co(II) and Ni(II) complexes with thiocyanate and (iso)nicotinic acid in which the carboxy groups act as both donors and acceptors to form extensive hydrogen bonds in their crystals.

## Experimental

All reagents were used as received. The CHN microanalyses were carried out with an ELEMENTAR vario EL elemental analyser. IR spectra (KBr pellets) were recorded on a PE-1710 FT-IR spectrometer. Thermogravimetry and differential scanning calorimetry were measured on a NETZSCH STA 409 PC system in flowing argon at a scanning rate of  $10^\circ\text{C min}^{-1}$ .

### Synthesis

#### $[\text{Co}(\mu\text{-NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$

An aqueous solution (20 ml) of  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (0.291 g, 1 mmol) and  $\text{NH}_4\text{SCN}$  (0.2 g, 2 mmol) was added to a warm aqueous solution (30 ml) of nicotinic acid (0.246 g, 2 mmol). The filtered solution was allowed to evaporate in a desiccator for one week to afford purple prismatic crystals in 70% yield. IR(KBr pellet):  $\nu = 3130$  w, 3060 w, 2999 w, 2837 w, 2681 w, 2564 w, 2110 vs, 1724 vs, 1635 m, 1599 s, 1535 m, 1424 s, 1382 s, 1330 m, 1296 s, 1196 m, 1115 m, 835 w, 820 m, 752 s, 692 s, 621 w, 565 w, 437 m  $\text{cm}^{-1}$ ; Anal. Calc. for  $\text{C}_{20}\text{H}_{15}\text{CoN}_5\text{O}_6\text{S}_2$  (544.42): C 44.1, H 2.8, N 12.9; Found: C 44.0, H 2.7, N 12.9%.

#### $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{isonicH})_2]\cdot(\text{isonicH})\cdot 2\text{H}_2\text{O}$

Green crystals of the title compound were prepared as for the previous compound, using  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  instead of  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ . Yield: 80%. IR(KBr pellet):  $\nu = 3579$  vs, 3443 s, 3108 w, 3074 w, 3000 w, 2894 w, 2654 w, 2519 w, 2103 vs, 1699 s, 1616 s, 1593 s, 1562 m, 1501 w, 1426 s, 1386 s, 1332 m, 1270 s, 1228 w, 1142 m, 1062 w, 1013 w, 940 w, 861 m, 848 m, 771 m, 707 w, 667 m, 544 w, 414 m  $\text{cm}^{-1}$ ; Anal. Calc. for  $\text{C}_{20}\text{H}_{15}\text{N}_5\text{NiO}_6\text{S}_2\cdot 4\text{H}_2\text{O}$  (616.26): C 39.0, H 3.8, N 11.4; Found: C 39.6, H 3.8, N 11.4%.

### X-ray crystallography

The intensity data were collected on a Rigaku RAXIS-RAPID IP diffractometer for the Co(II) complex and a Rigaku RAXIS IV IP diffractometer for the Ni(II) complex, with graphite-monochromated Mo K $\alpha$  radiation and corrected by “multi-scan” absorption corrections.<sup>13</sup> The structures were solved by direct methods and refined by least-squares on  $F^2$  using SHELXS and SHELXL programs.<sup>4</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-bound hydrogen atoms were treated as riding and were included in the refinement with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The acid H atoms of the Co(II) complex were similarly generated, and an  $sp^2$ -type of hybridisation was assumed. The acid H atoms, water H atoms and iminium H atom of Ni(II) compound were located in the difference Fourier map and included in the refinement; their  $U_{\text{iso}}$  values were set to  $1.5U_{\text{eq}}$  of their bound atoms.

The final difference Fourier map of the Co(II) compound had large peaks at about 1 Å from both cobalt atoms; these could not be attributed to a minor disorder component, and are probably an artifact. Nonetheless, the large peaks contributed to the high  $R$  index although the refined model is chemically reasonable in terms of bond dimensions and atomic displacement parameters.

*Crystal data for  $[\text{Co}(\mu\text{-NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$ :*  $M = 544.42$ , triclinic, space group  $P-1$ ,  $a = 7.2963(15)$ ,  $b = 11.287(2)$ ,  $c = 14.504(3)$  Å,  $\alpha = 108.74(3)$ ,  $\beta = 102.03(3)$ ,  $\gamma = 95.75(3)^\circ$ ,  $Z = 2$ ,  $V = 1088.1(4)$  Å<sup>3</sup>,  $\mu(\text{Mo K}\alpha) = 1.030$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.662$  Mg·m<sup>-3</sup>, 10 607 reflections collected (4945 unique,  $R_{\text{int}} = 0.0245$ ), 310 parameters, no restraint,  $R1 = 0.0774$ ,  $wR2 = 0.2748$  for 4075 reflections with  $I > 2\sigma(I)$ ,  $S = 1.143$ ,  $\Delta\rho_{\text{max}} = 3.204$  eÅ<sup>-3</sup>.

*Crystal data for  $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{isonicH})_2]\cdot(\text{isonicH})\cdot 2\text{H}_2\text{O}$ :*  $M = 616.26$ , monoclinic, space group  $C2/c$ ,  $a = 25.129(5)$ ,  $b = 7.4985(15)$ ,  $c = 14.522(3)$  Å,  $\beta = 108.84(3)^\circ$ ,  $Z = 4$ ,  $V = 2589.8(9)$  Å<sup>3</sup>,  $\mu(\text{Mo K}\alpha) = 0.973$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.581$  Mg·m<sup>-3</sup>, 4098 reflections collected (2340 unique,  $R_{\text{int}} = 0.0636$ ), 176 parameters, 6 restraints,  $R1 = 0.0576$ ,  $wR2 = 0.1388$  for 2141 reflections with  $I > 2\sigma(I)$ ,  $S = 1.153$ ,  $\Delta\rho_{\text{max}} = 0.495$  eÅ<sup>-3</sup>.

Crystal data reported in this paper have been deposited with Cambridge Crystallographic Data Centre (CCDC No. 650158 and 650159).

## Results and discussion

### Synthesis

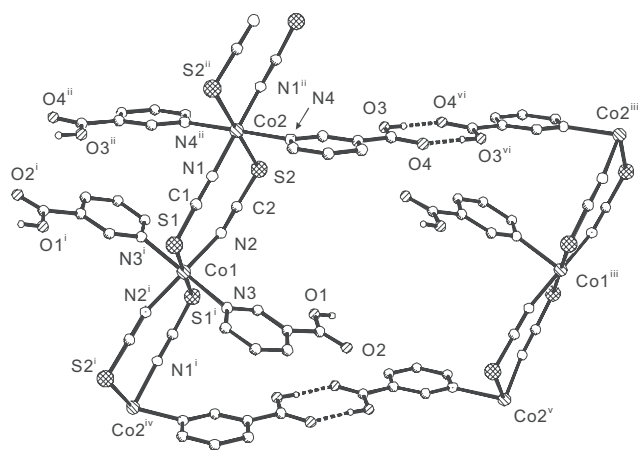
Slow evaporation of an aqueous solution of  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{SCN}$  and nicotinic acid in 1:2:2 molar ratio afforded purple prismatic crystals of  $[\text{Co}(\mu\text{-NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$ , whose structure was later determined by X-ray diffraction. However, when isonicotinic acid was used instead of nicotinic acid, no reaction occurred under the same experimental conditions. On the other hand, reactions of  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{SCN}$

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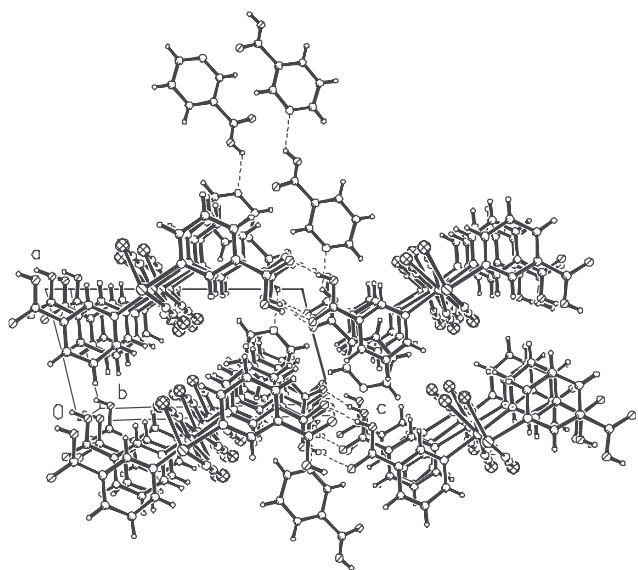
with either nicotinic acid or isonicotinic acid in 1:2:2 molar ratio gave green crystals. However, the crystals of the Ni–nicH complex are not suitable for X-ray diffraction and were not characterised further. Only the Ni–isonicH complex was studied in this paper.

#### Crystal structure of $[\text{Co}(\mu\text{-NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$

In the crystal, there are two types of crystallographically-independent cobalt(II) atoms which lie on inversion centres. Each cobalt(II) atom is coordinated by two pyridyl N atoms of two nicotinic acids, and two N atoms, two S atoms of four ambidentate  $\text{SCN}^-$  ligands in a *trans*-octahedral geometry. The Co–N( $\text{SCN}^-$ ) and Co–S bond lengths are comparable to those observed in a 2D H-bonded coordination network –  $[\text{Co}(\mu\text{-NCS})_2(4\text{-NH}_2\text{PhCOOH})]_n$ .<sup>5</sup> Each pair of adjacent metal atoms is bridged by two inversely related  $\mu\text{-NCS-S,N}$  ligands, resulting in a 1D chain of  $[\text{Co}(\text{NCS})_2]_n$  along the crystallographic *b*-axis. The remaining two *trans*-positions



**Fig. 1** Ball and stick diagram of the X-ray structure of one parallelogram cavity in  $[\text{Co}(\text{NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$ , showing the coordination environments around Co(1) and Co(2) atoms. Selected distances (Å): Co(1)–N(2) 2.064(5), Co(1)–N(3) 2.159(5), Co(1)–S(1) 2.6058(17), Co(2)–N(1) 2.066(5), Co(2)–N(4) 2.188(5), Co(2)–S(2) 2.5748(18), O3...O4<sup>vi</sup> 2.685(7). Symmetry codes: (i)  $-x, 2-y, 1-z$ ; (ii)  $-x, 1-y, 1-z$ ; (iii)  $x, y, z + 1$ ; (iv)  $x, y + 1, z$ ; (v)  $x, y + 1, z + 1$ ; (vi)  $-x, 1-y, 2-z$ .



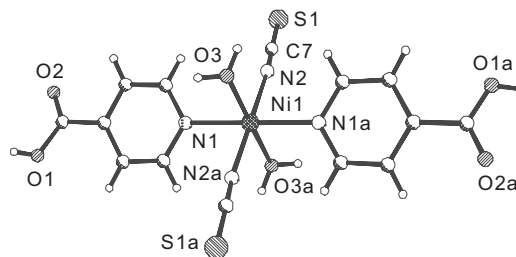
**Fig. 2** Packing diagram of  $[\text{Co}(\text{NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$  viewing along the *b*-axis.

around the Co-atoms are occupied by two N atoms of two nicotinic acids. Interestingly and importantly, each nicotinic acid coordinated to Co(2) forms a complimentary head-to-head double hydrogen bond  $[\text{O}(3)\dots\text{O}(4^{\text{vi}})]$  with the adjacent inversely related nicotinic acid, leading to 2D networks spreading over the *bc* plane with large parallelogram cavities ( $11.28 \times 14.50$  Å). On the other hand, nicotinic acids coordinated to Co(1) are tilted to the chain of  $[\text{Co}(\text{NCS})_2]_n$ , reducing the guest available space of the cavity (Fig. 1). Due the *meta*-positions of carboxy groups, the networks formed by linking 1D chains of  $[\text{Co}(\text{NCS})_2]_n$  via the H-bonded dimer of nicotinic acids are actually puckered, which are further packed to generate channels parallel to the *a*-axis. In each of these channels, reside two anti-parallel 1D chains of H-bonded uncoordinated nicotinic acids, which account for one-third of the pyridyl carboxy ligands per formula unit, as shown in Fig. 2. It is noteworthy that  $[\text{Co}(\mu\text{-NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$  is isostructural with our previously reported  $[\text{Cd}(\mu\text{-NCS})_2(\text{nicH})_2]\cdot(\text{nicH})$ . The similarity of the coordination geometries observed in these two complexes implies that Co(II) might be used, as an alternative choice, to replace Cd(II) in a  $\text{M}^{\text{II}}\text{-SCN}^-\text{-L}$  system.

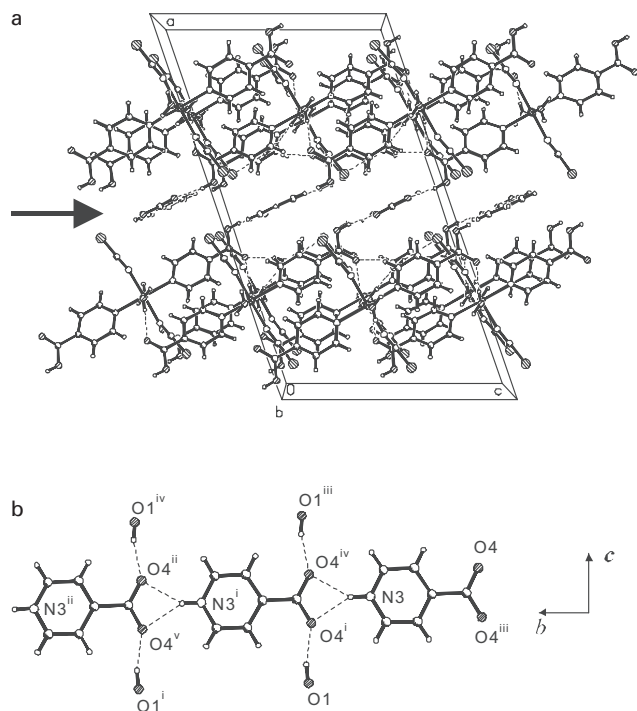
TG measurement indicated that the Co(II) complex is stable up to 210°C. From that point to 450°C, this complex experienced successive weight loss with three endothermic events at 228.4, 284.7 and 440°C, corresponding to the decomposition of this complex. The final residue at 500°C accounts for 19.4% of the total mass, which may be CoS or  $\text{Co}_2\text{S}_3$  according to the calculated residual weight percentages of 16.7% or 19.7%, respectively.

#### Crystal structure of $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{isonicH})_2]\cdot(\text{isonicH})\cdot 2\text{H}_2\text{O}$

Elemental analysis suggests an M/L ratio of 1:3 for this complex. X-ray analysis reveals that it is a discrete mononuclear complex; only two of the three isonicotinic acids per formula unit are coordinated to the central metal ion, the left one exists in the crystal lattice *via* hydrogen bonds. The Ni atom, seated in an inversion centre, is hexacoordinated by two aqua ligands, two isothiocyanates and two N-coordinated isonicotinic acids in a *trans*-octahedral geometry. In contrast to the Co(II) complex, isothiocyanates here serve as monodentate ligands. In the crystal, the mononuclear complexes and lattice water molecules form 2D layers spreading over the *bc* plane (Fig. 4a) The uncoordinated isonicotinic acids exist as zwitter-ions and form 1D chains along the *b*-axis *via* symmetric N–H...O H-bonds (Fig. 4b), which are intercalated between these layers *via* O–H...O H-bonds, as indicated by the arrow in Fig. 4a. We note that Sekiya *et al.* reported that in *acetoneitrile* they could obtain a series of complexes with 2D H-bonded networks featuring  $[\text{Ni}(\text{SCN})_2]_n$  chains and the H-bonded



**Fig. 3** Ball-and-stick diagram of the X-ray structure of mononuclear  $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{isonicH})_2]$ . Selected distances (Å): Ni(1)–N(1) 2.136(3), Ni(1)–N(2) 2.047(4), Ni(1)–O(3) 2.093(3); N(2)–Ni(1)–N(1) 89.53(13), O(3)–Ni(1)–N(1) 90.61(11), N(2)–Ni(1)–O(3) 91.64(13). Symmetry codes: (a)  $-x-1/2, -y-1/2, -z-1$ .



**Fig. 4** (a) Packing diagram of  $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{isonicH})_2] \cdot (\text{isonicH}) \cdot 2\text{H}_2\text{O}$  viewing along the  $b$ -axis. The arrow points to the layer of uncoordinated isonicotinic acids in the crystal. (b) A view of the H-bonded chain of isonicotinic acids. Hydrogen bonds (Å):  $\text{N}(3) \cdots \text{O}(4^i)$  2.876(5),  $\text{O}(1) \cdots \text{O}(4^i)$  2.655(4). Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $x, y + 2, z$ ; (iii)  $-x + 1, y, -z + 1/2$ ; (iv)  $-x + 1, y + 1, -z + 1/2$ ; (v)  $-x + 1, y + 2, -z + 1/2$ .

dimer of isonicH.<sup>3</sup> On the other hand, we only obtained a mononuclear Ni(II) complex when the reaction was conducted in water. Comparing the coordination sphere around the Ni(II) atom in these complexes, we think that

$[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{isonicH})_2]$  could be regarded as the precursor for Sekiya's 2D networks. In this case, the reaction solvent may play an important role in determining the final products: reaction in water favours the coordination of water molecules and the mononuclear complex dominates; while reaction in a nonaqueous solvent like acetonitrile would facilitate the dissociation of aqua ligands and the further coordination of S-atoms of thiocyanates, leading to the polymerisation of the mononuclear complex to give  $[\text{Ni}(\text{NCS})_2]_n$  chains.

The TGA curve of the Ni(II) complex showed the first weight loss in the range 97–180°C with an endothermic event at 125°C, corresponding to the release of four water molecules (observed, 13.2%; calculated, 11.7%). Following were several weight losses until 450°C with three endothermic events at 279.7, 372.8 and 440.5°C, amounting to 71.4% of the total mass, corresponding to the decomposition of this complex. The final residue at 500°C may possibly be NiS (observed, 15.4%; calculated, 14.7%).

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