

catena-Poly[[bis(nicotinamide- κN^1)-copper(I)]- μ -thiocyanato- $\kappa^2 N:S$]

Christian Näther* and Inke Jeß

 Institut für Anorganische Chemie, Christian Albrechts Universität Kiel,
 Olshausenstraße 40, D-24098 Kiel, Germany
 Correspondence e-mail: cnaether@ac.uni-kiel.de

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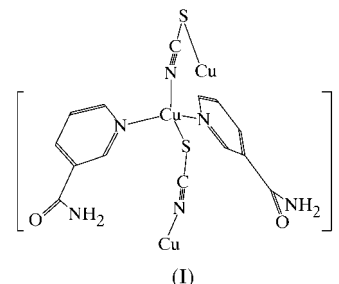
The Cu^{I} cations in the title compound, $[\text{Cu}(\text{NCS})(\text{C}_6\text{H}_6\text{-N}_2\text{O})_2]_n$, are coordinated by N atoms from each of two mirror-related nicotinamide ligands, as well as by one N atom of one thiocyanate ligand and one S atom of a symmetry-related thiocyanate ligand, within a slightly distorted tetrahedron. The Cu^{I} cations and the thiocyanate anions are located on a crystallographic mirror plane and the nicotinamide ligands occupy general positions. The Cu^{I} cations are connected by the thiocyanate anions to form chains in the direction of the crystallographic a axis. These chains are connected by hydrogen bonds between the amide H atoms and the O atoms of adjacent nicotinamide ligands, to give a three-dimensional structure.

Comment

Coordination polymers based on copper(I) halides or pseudohalides and aromatic amine ligands show great structural diversity. The copper(I) halides and pseudohalides form typical inorganic substructures, such as dimers, single and double chains, or helical structures, which are linked by the amine ligands to give multidimensional coordination polymers (Blake *et al.*, 1999; Kromp & Sheldrick, 1999; Teichert & Sheldrick, 1999, 2000; Graham *et al.*, 2000; Roßenbeck & Sheldrick, 2000; Näther & Greve, 2001; Näther & Jeß, 2001; Persky *et al.*, 2001).

The dimensionality of such coordination polymers depends predominantly on the coordination behaviour of the organic ligands. If the amine ligand contains two N atoms that are bound to two different Cu^{I} cations, mostly two- and three-dimensional structures are observed. A different strategy to connect the CuX substructures (X is Cl, Br, I, SCN or CN) is hydrogen bonding between the organic amine ligands, which are linked to the CuX substructures by N coordination. In this case, the amine ligands must contain hydrogen-bond donor and/or acceptor groups, such as nicotinamide or isonicotinamide. These compounds have been used, for example, for the preparation of some coordination polymers based on chromium-arene compounds (Brammer *et al.*, 2000). Starting from

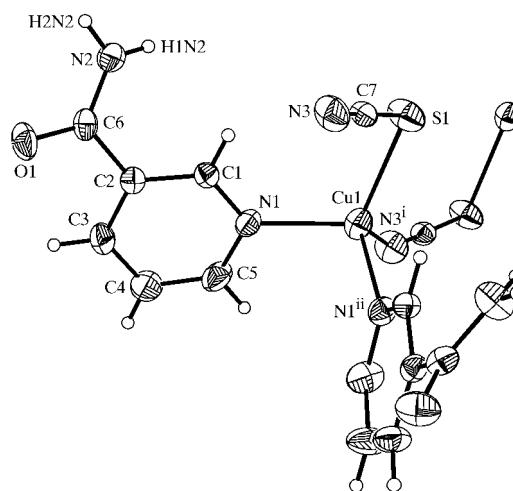
these results, we prepared crystals of the title compound, (I), by the reaction of $\text{Cu}^{\text{I}}\text{SCN}$ with nicotinamide in acetonitrile. According to a search of the Cambridge Structural Database (CSD; *CONQUEST* Version 1.3, 2001; Allen & Kennard, 1993), the only previously known copper complexes with nicotinamide are those involving Cu^{II} .



In the crystal structure of (I), the Cu^{I} atoms are coordinated by the N atom from one thiocyanate ligand, the S atom from a symmetry-related thiocyanate ligand and an N atom from each of two nicotinamide ligands, which are related by a crystallographic mirror plane that passes through the Cu^{I} atoms and the thiocyanate ligands (Fig. 1).

The $\text{Cu}-\text{N}$ and $\text{Cu}-\text{S}$ bond lengths in (I) are within the range found in comparable Cu^{I} complexes retrieved from the CSD. The $X-\text{Cu}-X$ angles are between $108.10(8)$ and $112.46(6)^\circ$, and the coordination polyhedron around the Cu^{I} cation can therefore be described as a slightly distorted tetrahedron. The Cu^{I} cations are connected by the thiocyanate ligands *via* $\mu\text{-N:S}$ coordination to form single ribbon-like chains which run in the direction of the crystallographic a axis. A similar CuSCN substructure is found in the crystal structure of poly[$\text{CuSCN}(\mu\text{-2-methylpyrazine})$] (Teichert & Sheldrick, 1999).

The CuSCN chains are connected by the nicotinamide ligands, *via* $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between the O atoms


Figure 1

A view of (I) showing the coordination of the Cu^{I} atom and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (ii) $x, \frac{1}{2} - y, z$].

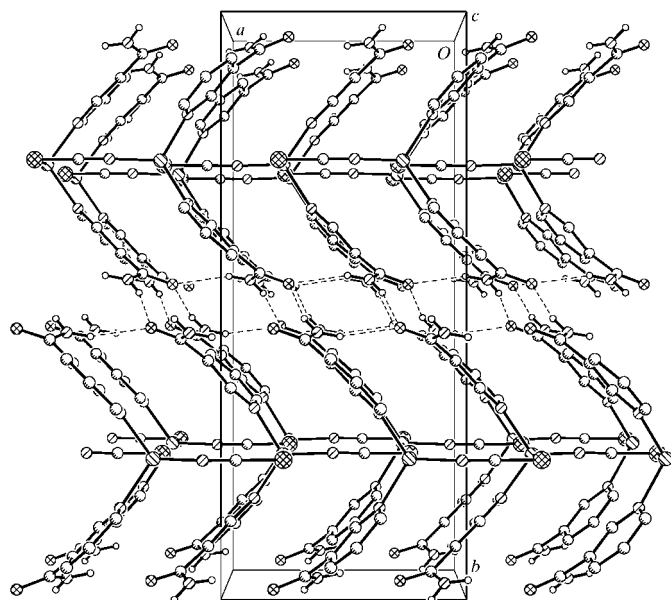


Figure 2

The crystal structure of (I) viewed down (010). Hydrogen bonds are shown as dashed lines and the H atoms bonded to C atoms have been omitted for clarity.

and the amide H atoms of adjacent nicotinamide ligands. The O atom acts as an acceptor for two different hydrogen bonds and both amide N atoms are involved as donors. Two O atoms and two amide NH₂ groups of four different nicotinamide ligands form nearly planar eight-membered rings, which are located around centres of inversion. Because the nicotinamide ligand is hydrogen bonded to two further nicotinamide ligands from two neighbouring CuSCN chains, a three-dimensional 'loop structure' is formed.

The observed hydrogen-bonding pattern is different from that in other nicotinamide coordination polymers, such as [Pt(nicotinamide)Cl₂] (Brammer *et al.*, 2000). In this latter compound, the nicotinamide ligand is connected only to one further ligand, by two N—H···O hydrogen bonds within a six-membered ring. Another complex in which Cu^ISCN coordination polymers are connected *via* hydrogen bonds between the ligands is *catena*-poly[(μ-thiocyanato)bis(4-hydroxypyrimidine)copper(I)] (Teichert & Sheldrick, 2000). In this compound, 'zigzag-like' CuSCN chains are also found. In contrast with (I), only a single O—H···N hydrogen bond is found between the hydroxy H atom and the uncoordinated pyrimidine N atom. In this compound, a loop structure is also found which is very similar to that in (I). However, the results presented here show that hydrogen bonding is a useful tool to expand the dimensionality in such Cu^I coordination polymers.

Experimental

The title compound was prepared by the reaction of nicotinamide (Acros; 122.13 mg, 1 mmol) and copper(I) thiocyanate (Alfa; 121.62 mg, 1 mmol) in acetonitrile (4 ml) at room temperature in a glass container. The reaction mixture was stirred for 1 d, and the resulting light-yellow precipitate of (I) was filtered off and washed

with water (yield 90.3%). The compound was shown to be phase pure by X-ray powder diffraction. For the preparation of single crystals of (I), the reaction mixture was not stirred.

Crystal data

[Cu(NCS)(C₆H₆N₂O)₂]
M_r = 365.88
 Orthorhombic, *Pnma*
a = 8.9304 (4) Å
b = 21.3533 (12) Å
c = 7.5895 (3) Å
V = 1447.27 (12) Å³
Z = 4
D_x = 1.679 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 8000 reflections
 θ = 3–26°
 μ = 1.67 mm⁻¹
T = 293 (2) K
 Block, yellow
 0.12 × 0.09 × 0.05 mm

Data collection

Stoe IPDS diffractometer
 φ scans
 11 282 measured reflections
 1446 independent reflections
 1172 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.044
 θ_{\max} = 26°
h = -10 → 10
k = -26 → 26
l = -9 → 9

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.078$
S = 1.10
 1446 reflections
 107 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.7777P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0084 (9)

Table 1

Selected geometric parameters (Å, °).

Cu1—N3 ⁱ	1.963 (3)	Cu1—S1	2.3261 (11)
Cu1—N1	2.0848 (18)		
N3 ⁱ —Cu1—N1	108.10 (8)	N3 ⁱ —Cu1—S1	112.15 (10)
N1 ⁱⁱ —Cu1—N1	103.05 (10)	N1—Cu1—S1	112.46 (6)

Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (ii) $x, \frac{1}{2} - y, z$.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H1N2···O1 ⁱ	0.86	2.18	3.003 (3)	159
N2—H2N2···O1 ⁱⁱ	0.86	2.13	2.959 (3)	163

Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (ii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$.

All H atoms were located in a difference Fourier map. Aromatic H atoms were positioned with idealized geometry and refined using a riding model, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The positions of the amide H atoms were taken from a difference Fourier map and were then refined as rigid groups, with N—H = 0.86 Å and *U*_{iso}(H) = 1.5*U*_{eq}(N).

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1135). Services for accessing these data are described at the back of the journal.

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