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Poly[[(pyridazine-κN)copper(I)]-μ_3-thiocyanato-$\kappa^3 N$:*S*:*S*]

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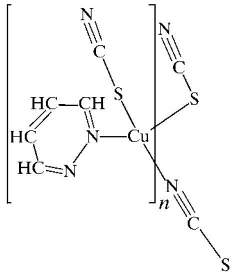
In the crystal structure of the title compound, $[Cu(NCS)(C_4H_4N_2)]_n$, each Cu atom is coordinated by one N atom of one pyridazine ligand and by one N and two S atoms of three symmetry-related thiocyanate anions within a distorted tetrahedron. Only one N atom of the pyridazine ligand is involved in Cu coordination. The Cu atoms are connected *via* the thiocyanate anions, forming layers parallel to the *ab* plane.

Comment

Recently, we have investigated coordination polymers based on copper(I) halides and pseudohalides and aromatic dinitrogen donor ligands (Näther *et al.*, 2002; Näther & Jeß, 2002, 2003; Näther, Wriedt & Jeß, 2003; Näther, Jeß *et al.*, 2003; Näther, Greve *et al.*, 2003). In these compounds, typical Cu*X* substructures occur, which are mostly connected by donor ligands. However, in some cases, the dinitrogen ligand does not bridge different Cu atoms. Frequently, for one particular copper(I) halide or pseudohalide, several compounds are found which differ in their ratio between the inorganic and organic parts; therefore, for example, 1:1, 2:1, 4:1 or 3:2 compounds are found.

We have found that most of amine-rich coordination polymers can be transformed into amine-poor coordination polymers *via* a well directed thermal decomposition. Therefore, we have begun systematic investigations of the synthesis, structure and thermal properties of such compounds. In some of these investigations, we were particularly interested in copper(I) thiocyanate compounds with aromatic dinitrogen ligands such as pyrazine, pyrimidine and pyridazine. With pyrimidine and pyrazine, only the 2:1 compound *catena*-[bis(μ_3-thiocyanato)(μ_2-pyrimidine)dicopper(I)] (Barnett *et al.*, 2000; Teichert & Sheldrick, 2000), the 1:1 compound *catena*-[(μ_2-thiocyanato)(μ_2-pyrazine)copper(I)] (Goher & Mautner, 1999) and the 2:1 compound *catena*-[bis(μ_2-thiocyanato)(μ_2-pyrimidine)dicopper(I)] (Blake *et al.*, 1998, 1999) have been reported. However, with pyridazine as the ligand, no structures have been reported to date. Against this background, we present here the structure of the title compound, (I), with pyridazine as the ligand.



(I)

In the structure of (I), the Cu atom is coordinated by one N atom of the pyridazine ligand, and one N atom and two S atoms of three symmetry-related thiocyanate ligands. Only one of the two pyridazine N atoms is involved in Cu coordination; the second N atom is not involved in any interaction.

As expected, the Cu—N bond length to the negatively charged thiocyanate anion is significantly shorter than that to the neutral pyridazine ligand. However, the bond lengths and angles around the Cu atom are comparable with those observed in other copper(I) thiocyanate coordination polymers with aromatic dinitrogen ligands (Barnett *et al.*, 2000; Teichert & Sheldrick, 2000; Goher & Mautner, 1999; Blake *et al.*, 1998, 1999), and the coordination polyhedron around the Cu atom can be described as a distorted tetrahedron.

In contrast with most other Cu*X* coordination polymers (where *X* is Cl, Br, N, SCN or CN), compound (I) contains an unusual Cu*X* substructure. The Cu atoms are connected *via* the S atoms of the thiocyanate anions into zigzag-like single chains which are elongated in the direction of the *a* axis. These Cu atoms are oriented in the direction of the lone pairs of the S atoms. These single chains are connected *via* the N atoms of the thiocyanate anions into layers which are parallel to the *ab* plane. As expected, the Cu atoms are oriented in the direction of the N—C—S vector. Only one of the two N atoms of the pyridazine ligand is involved in Cu coordination. It must be noted that a similar coordination network is also found in *catena*-[(μ_3-thiocyanato-*N*:*S*:*S*)pyridylcopper] and *catena*-[(μ_3-thiocyanato-*N*:*S*:*S*)pyridylsilver] (Krautscheid *et al.*, 1998). These compounds are not isomorphous with (I), but the topology of the coordination network is similar. Concerning the notation of these compounds, those authors use the term *catena*, whereas we use poly because the compounds exhibit a layered structure.

In contrast with (I), in the 1:1 compound *catena*-[(μ_2-thiocyanato)(μ_2-pyrazine)copper(I)] (Goher & Mautner, 1999), which exhibits the same ratio of copper(I) thiocyanate and the N-donor ligand, a Cu*X* substructure is found which is frequently observed in such coordination polymers with CuCl, CuBr or CuI. Cu*X* single chains are observed which are connected into layers by the dinitrogen ligands. In that structure, the N-donor ligand acts as a bridging ligand and the S atoms of the thiocyanate anions are coordinated to only one

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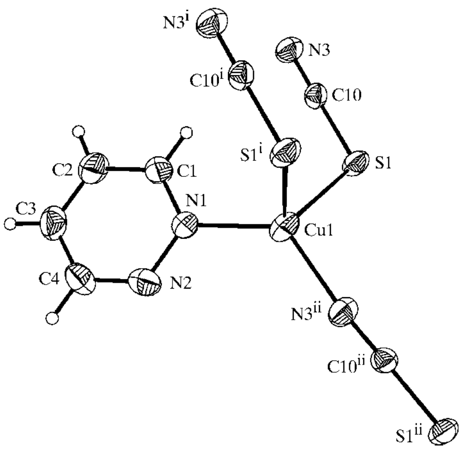

Figure 1

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

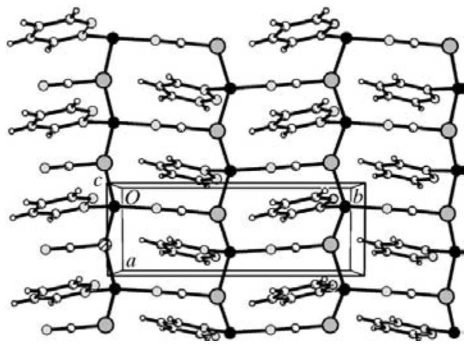

Figure 2

The crystal structure of (I), viewed along the crystallographic c axis.

Cu atom. This clearly shows the influence of the position of the N-donor atoms on the topology of the coordination network. It is interesting to note that that compound also crystallizes in the chiral space group $P2_1$. Because of the different stoichiometry, the structures of the amine-poor 2:1 compounds *catena*-[bis(μ_3-thiocyanato)(μ_2-pyrimidine)dicopper(I)] (Barnett *et al.*, 2000) and *catena*-[bis(μ_2-thiocyanato)(μ_2-pyrimidine)-dicopper(I)] (Blake *et al.*, 1998, 1999) cannot be compared with that of (I).

Concerning the thermal behaviour of (I), we have found that no amine-poor coordination polymers can be observed on heating. If (I) is heated in a thermobalance starting at about 483 K, a mass loss is observed which corresponds to the loss of all the amine ligands. The final product of this thermal decomposition reaction was identified as copper(I) thiocyanate by X-ray powder diffraction.

Experimental

The title compound was prepared by the reaction of CuSCN (0.1 mmol) and pyridazine (0.1 mmol) in acetonitrile (4 ml) in a Teflon-lined steel autoclave at 373 K. After 3 d, the reaction mixture was cooled, and the product was filtered off and washed with ethanol and diethyl ether. The homogeneity of the product was checked by comparison of the experimental powder pattern with that calculated from the single-crystal data. In addition, the CHN content obtained by elemental analysis was in agreement with that calculated.

Crystal data

[Cu(NCS)($C_4H_4N_2$)]
M_r = 201.71
Monoclinic, $P2_1$
a = 3.8338 (7) Å
b = 10.5755 (12) Å
c = 8.3938 (12) Å
β = 96.182 (14)°
V = 338.34 (9) Å^3
Z = 2
D_x = 1.980 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 104 reflections
θ = 15–20°
μ = 3.45 mm^{-1}
T = 293 (2) K
Block, yellow
0.12 × 0.09 × 0.08 mm

Data collection

Stoe AED-II diffractometer
ω scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
$T_{\min}$ = 0.698, $T_{\max}$ = 0.757
2193 measured reflections
1943 independent reflections
1620 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 30.0°
$h = 0 \rightarrow 5$
$k = -14 \rightarrow 13$
$l = -11 \rightarrow 11$
4 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.062
S = 1.06
1943 reflections
93 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2 + 0.0638P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.34 e Å^{-3}
$\Delta\rho_{\min}$ = −0.49 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.021 (3)

Table 1

Selected geometric parameters (Å, °).

Cu1—N3^{i}	1.930 (3)	Cu1—S1^{ii}	2.4053 (9)
Cu1—N1	2.012 (2)	Cu1—S1	2.4299 (9)
N3^{i}—Cu1—N1	126.44 (10)	C10—S1—Cu1^{iii}	101.44 (9)
N3^{i}—Cu1—S1^{ii}	107.10 (8)	C10—S1—Cu1	109.92 (9)
N1—Cu1—S1^{ii}	105.42 (8)	Cu1^{iii}—S1—Cu1	104.91 (3)
N3^{i}—Cu1—S1	101.34 (8)	C10—N3—Cu1^{iv}	174.2 (2)
N1—Cu1—S1	109.88 (8)	C1—N1—Cu1	122.72 (19)
S1^{ii}—Cu1—S1	104.91 (3)	N2—N1—Cu1	117.6 (2)

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

H atoms were positioned with idealized geometry (C—H distances of 0.93 Å) and refined with fixed isotropic displacement parameters [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$] using a riding model. The absolute structure could not be determined using the Flack x test (Flack, 1983); therefore, a twin refinement for racemic twinning was performed, yielding a BASF parameter of 0.33 (2). However, if no twin refinement was performed, the reliability factors were different for a refinement using the current setting [wR_2 = 0.0722, R_1 for $F_o > 4\sigma(F_o)$ = 0.0313] and for the inverse structure [wR_2 = 0.1006, R_1 for $F_o > 4\sigma(F_o)$ = 0.0388].

Data collection: *DIF*4 (Stoe & Cie, 1990); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-NT* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1232). Services for accessing these data are described at the back of the journal.

References

Barnett, S. A., Blake, A. J., Champness, N. R. & Wilson, C. (2000). *CrystEngComm*, Article No. 5, pp. 36–40.

Blake, A. J., Brooks, N. R., Champness, N. R., Crew, M., Hanton, L. R., Hubberstey, P., Parsons, S. & Schroder, M. J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2813–2817.

Blake, A. J., Champness, N. R., Crew, M., Hanton, L. R., Parsons, S. & Schroder, M. (1998). *J. Chem. Soc. Dalton Trans.* pp. 1533–1534.

Bruker (1998). *SHELXTL-NT*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Goher, M. A. S. & Mautner, F. A. (1999). *Polyhedron*, **18**, 1805–1810.

Krautscheid, H., Emig, N., Klaassen, N. & Seringer, P. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3071–3077.

Näther, C., Greve, J. & Jeß, I. (2002). *Solid State Sci.* **4**, 813–820.

Näther, C., Greve, J., Jeß, I. & Wickleder, C. (2003). *Solid State Sci.* **5**, 1167–1176.

Näther, C. & Jeß, I. (2002). *J. Solid State Chem.* **169**, 103–112.

Näther, C. & Jeß, I. (2003). *Inorg. Chem.* **42**, 2968–2976.

Näther, C., Jeß, I., Lehnert, N. & Hinz-Hübner, D. (2003). *Solid State Sci.* **5**, 1343–1357.

Näther, C., Wriedt, M. & Jeß, I. (2003). *Inorg. Chem.* **42**, 2391–2397.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Stoe & Cie (1990). *DIF*4 (Version 7.09X/DOS) and *REDU*4 (Version 7.03). Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1998). *X-SHAPE*. Version 1.03. Stoe & Cie, Darmstadt, Germany.

Teichert, O. & Sheldrick, W. S. (2000). *Z. Anorg. Allg. Chem.* **626**, 2196–2202.