Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A novel thiocyanate-bridged one-dimensional chain complex: $[Cu(NCS)_2(Hambi)]$ (Hambi is 2-aminomethyl-1*H*-benzimidazole)

Yun-Bo Jiang, Hui-Zhong Kou,* Fei Gao and Ru-Ji Wang

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China
Correspondence e-mail: kouhz@mail.tsinghua.edu.cn

Received 15 March 2004
Accepted 16 April 2004
Online 22 May 2004

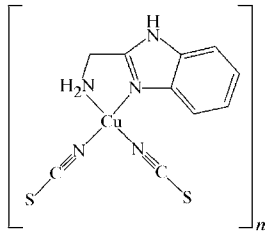
Using 2-aminomethyl-1*H*-benzimidazole as the ligand, a new thiocyanate-bridged copper(II) complex, namely bis(2-aminomethyl-1*H*-benzimidazole-κ^2N^2,N^3)dithiocyanatocopper(II), $[Cu(NCS)_2(C_8H_9N_3)]$, has been synthesized and structurally characterized. The Cu atom is five-coordinated and exhibits a distorted square-pyramidal geometry. The thiocyanate ions (NCS^-) act as either bridging or terminal ligands. The bridging NCS^- ligands connect neighboring Cu atoms, constructing chains, while the terminal NCS^- ligands form hydrogen bonds with amine H atoms, leading to a complicated network.

Comment

2-Aminomethyl-1*H*-benzimidazole (Hambi) is a bidentate ligand that can coordinate to metal ions *via* two N atoms. The complex of cobalt(III) and ambi has been synthesized but has not been structurally characterized by X-ray diffraction analysis (Gable *et al.*, 1996). However, the crystal structure of the mixed-ligand cobalt(III) complex with Hambi and $acac^-$ has been reported (Cardwell *et al.*, 1997), and the mixed-ligand copper(II) complex with Hambi and iminodiacetate (de la Cueva *et al.*, 1998), and the nickel–Hambi/$ambi^-$ (He *et al.*, 2002) and copper–Hambi–dicyanamide (He *et al.*, 2003) complexes, have also been prepared and their structures determined.

Thiocyanate, NCS^-, is a versatile pseudohalogen ligand that is commonly observed to bridge metal ions. A considerable number of double thiocyanate-bridged copper(II) complexes have been reported (Julve *et al.*, 1993; Liu *et al.*, 2003); however, single thiocyanate-bridged complexes are comparatively rare (Moustarder *et al.*, 2000; Cano *et al.*, 2000; Karan *et al.*, 2002). We report here the crystal structure of the title copper(II) complex with Hambi and thiocyanate, (I).

A displacement ellipsoid drawing of the title complex is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. According to Brophy *et al.* (1999), the coordination geometry about the Cu atom is that of a slightly distorted square pyramid ($\tau = 0.126$), with one N atom from each of the pendant aminomethyl group, the imidazole ring, the terminal thiocyanate ligand and the bridging thiocyanate ion defining the basal plane, and with one S atom from another bridging



(I)

thiocyanate ligand occupying the apical position [Cu1—S2A = 2.942 (1) Å; symmetry code: (A) $x, \frac{1}{2}-y, z-\frac{1}{2}$]. The Cu atom lies 0.0393 (4) Å above the basal plane, towards the apical S2A atom, suggesting the presence of a weak Cu···S coordination interaction. A thiocyanate-bridged chain-like structure results. The chains are connected by interchain S···H—N hydrogen bonds, giving rise to a wave-shaped layer. As shown in Fig. 1, atom S1 of the terminal thiocyanate ligand interacts with an H atom of the pendant aminomethyl group of a neighboring chain, with an S···H distance of 2.64 Å and an S···H—N angle of 137°. At the same time, atom S1 exhibits a hydrogen-bonding interaction with the intrachain primary amine H atom (S···H = 2.58 Å and S···H—N = 175°). Atom S2 of the bridging NCS^- ion is also involved in hydrogen bonding with

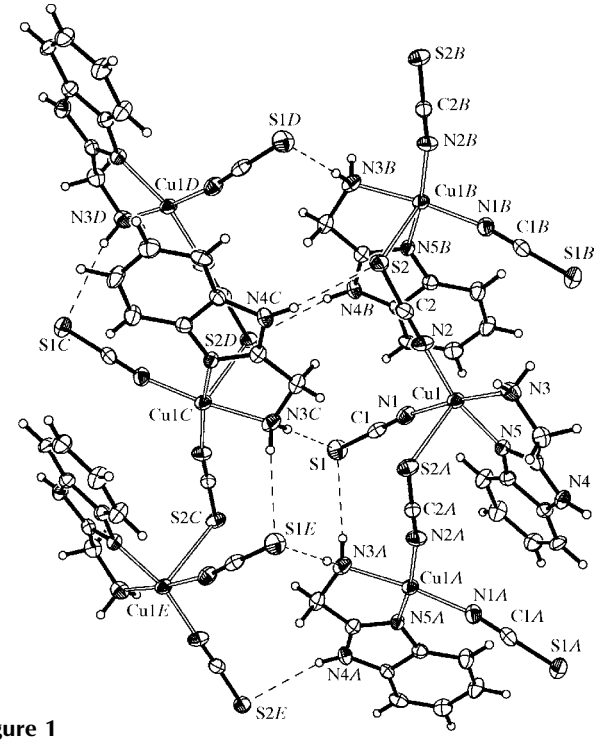


Figure 1
A view of (I), showing two hydrogen-bonded chains. Displacement ellipsoids are drawn at the 30% probability level. Cu, S and N atoms are shown with octant shading. [Symmetry codes: (A) $x, \frac{1}{2}-y, z-\frac{1}{2}$; ($B$) $x, \frac{1}{2}-y, z+\frac{1}{2}$; ($C$) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; ($D$) $1-x, -y, 1-z$; (E) $-x, 1-y, -z$.]

 DOI: 10.1107/S0108270104009102

the H atom attached to the benzimidazole N atom of an adjacent chain (S···H = 2.58 Å and S···H—N = 150°).

The title complex is unlike the dicyanamide-bridged Cu^{II} analogue $Cu(Hambi)(dca)_2$ (dca^- is the dicyanamide anion; Kou & He, 2003) in that no π–π contacts between conjugated benzimidazole cycles of the Hambi ligands are observed in (I). This difference may be due to the existence of different interchain hydrogen bonding in the two complexes.

Experimental

A solution (5 ml) of $CuCl_2{\cdot}4H_2O$ (20.6 mg, 0.1 mmol) in water was added to an aqueous solution (5 ml) of Hambi·2HCl (22.1 mg, 0.1 mmol). Blue microcrystals were obtained by adding KSCN (19.6 mg, 0.2 mmol) dissolved in a minimum volume of water. Acetonitrile (~5 ml) was added until all of the precipitate had dissolved. The mixture was filtered and the filtrate was evaporated slowly, generating blue–green needle-shaped single crystals suitable for X-ray diffraction analysis (yield 60%).

Crystal data

$[Cu(NCS)_2(C_8H_9N_3)]$
M_r = 326.88
Monoclinic, $P2_1/c$
a = 9.522 (3) Å
b = 12.707 (4) Å
c = 10.757 (3) Å
β = 99.418 (6)°
V = 1284.0 (7) Å^3
Z = 4
D_x = 1.691 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1428 reflections
θ = 2.5–25°
μ = 2.01 mm^{-1}
T = 293 (2) K
Prism, blue
0.14 × 0.10 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.708, T_{max} = 0.886
6534 measured reflections
2257 independent reflections
1428 reflections with $I > 2\sigma(I)$
R_{int} = 0.073
θ_{max} = 25.0°
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 12$
$l = -12 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.085
S = 0.92
2257 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.029P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

All H atoms were found in difference maps, and were then positioned using the HFIX command in *SHELXL*97 (Sheldrick, 1997) and allowed for as riding atoms (C—H = 0.97 Å and N—H = 0.86 Å).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.935 (4)	S2—C2	1.630 (5)
Cu1—N2	1.938 (4)	S1—C1	1.625 (6)
Cu1—N5	1.970 (4)	N1—C1	1.154 (6)
Cu1—N3	2.022 (4)	N2—C2	1.158 (5)
Cu1—S2^{i}	2.942 (1)		
N1—Cu1—N2	94.68 (17)	N2—Cu1—N3	89.38 (16)
N1—Cu1—N5	95.35 (16)	N5—Cu1—N3	81.33 (16)
N2—Cu1—N5	166.60 (17)	N2—C2—S2	178.4 (5)
N1—Cu1—N3	174.14 (17)	N1—C1—S1	178.9 (5)

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

This work was supported by the Natural Science Foundation of China (grant Nos. 20201008 and 50272034).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1155). Services for accessing these data are described at the back of the journal.

References

Brophy, M., Murphy, G., O'Sullivan, C., Hathaway, B. & Murphy, B. (1999). *Polyhedron*, **18**, 611–613.
Bruker (2000). *SMART* and *SAINT* (Versions 5.6), and *SADABS* (Version 2.01). Bruker AXS Inc., Madison, Wisconsin, USA.
Cano, J., Diaz, C., Solans, X. & Font-Bardia, M. (2000). *Inorg. Chem.* **39**, 1611–1614.
Cardwell, T. J., Edwards, A. J., Hartshorn, R. M., Holmes, R. J. & McFadyen, W. D. (1997). *Aust. J. Chem.* **50**, 1009–1015.
Cueva, I. S. de la, Sicilia, A. G., Gonzalez, J. M., Bugella, E., Castineiras, A. & Niclos-Gutierrez, J. (1998). *React. Funct. Polym.* **36**, 211–216.
Gable, R. W., Hartshorn, R. M., McFadyen, W. D. & Nunno, L. (1996). *Aust. J. Chem.* **49**, 625–632.
He, Y., Kou, H. Z., Wang, R. J. & Li, Y. D. (2003). *Transition Met. Chem.* **28**, 464–467.
He, Y., Kou, H. Z., Zhou, B. C., Xiong, M., Wang, R. J. & Li, Y. D. (2002). *Acta Cryst.* E**58**, m389–m391.
Julve, M., Verdaguer, M., de Munno, G., Real, J. A. & Bruno, G. (1993). *Inorg. Chem.* **32**, 795–802.
Karan, N. K., Mitra, S., Matsushita, T., Gramlich, V. & Rosair, G. (2002). *Inorg. Chim. Acta*, **332**, 87–91.
Kou, H.-Z. & He, Y. (2003). *Chem. Lett.* **32**, 902–904.
Liu, J. C., Guo, G. C., Huang, J. S. & You, X. Z. (2003). *Inorg. Chem.* **42**, 235–243.
Moustarder, S. L., Hudhomme, P., Durand, C., Mercier, N., Azcondo, M. T., Delhaes, P., Riou, A. & Gorgues, A. (2000). *J. Mater. Chem.* **10**, 617–623.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Spek, A. L. (2002). *PLATON*. Version of 2002. University of Utrecht, The Netherlands.