

Poly- μ -2,5-dimethylpyrazine- μ -dithiocyanato-*N*, *S,S*-dicopper(I): a three-dimensional coordination polymer containing both molecular and anionic rod ligands

Tom Otieno,^{(1)*} Jaime R. Blanton,⁽¹⁾ Kena J. Lanham,⁽¹⁾ and Sean Parkin⁽²⁾

Received July 1, 2002

Reaction of CuSCN with 2,5-dimethylpyrazine (2,5-me₂pyz) yields a polymeric material, [Cu₂(SCN)₂(2,5-me₂pyz)]_∞, which has been crystallographically characterized. The compound crystallizes in the monoclinic space group *P*2₁/*n* with *a* = 5.6850(2) Å, *b* = 6.92877(3) Å, *c* = 14.3575(6) Å, β = 93.435(1)°, and *Z* = 2. It contains [Cu(SCN)]_∞ sheets in which each thiocyanate ligand acts in a μ -*N,S,S*-bridging mode. The sheets are bridged by 2,5-dimethylpyrazine ligands to generate a three dimensional network. The compound has also been characterized by infrared spectroscopy and thermogravimetric analysis.

KEY WORDS: Copper(I) thiocyanate; 2,5-dimethylpyrazine; coordination polymer.

Introduction

Crystal engineering of coordination polymers is of great current research interest because it offers the potential for the rational design and synthesis of new materials with, for example, novel structural, electronic, magnetic, and catalytic properties.¹⁻³ Despite the great strides made in the design and synthesis of coordination polymers, many factors such as the nature of the metal and ligand, solvent, temperature, and metal to ligand mole ratio influence reactions and it is still not possible to always predict the structures of the products on the basis of the components present in

the reaction mixture. In order to achieve improved structural control, more exploratory work has to be done in this area.

The generation of infinite-ordered frameworks may be achieved by linking together tetrahedral or octahedral metal centers through rod-like connecting ligands, such as pyrazine.⁴ Copper(I) is a suitable candidate for pyrazine and its derivatives because, as a soft acid, it favors coordination to soft bases such as ligands containing nitrogen and sulfur atoms. Lever *et al.*^{5,6} prepared the first copper(I)-pyrazine complexes in the early 1960s, but it was not until 1989 that we reported the first X-ray structural study of a pyrazine-bridged copper(I) polymer.⁷ Since then the number of structural studies of one-, two-, and three-dimensional coordination polymers of copper(I) with pyrazine and its methyl substituted derivatives has continued to grow.⁸⁻²⁵ As part of our ongoing research in this area, we report here the synthesis and structural, spectral, and thermal

⁽¹⁾Department of Chemistry, Eastern Kentucky University, Richmond, Kentucky 40475-3102.

⁽²⁾Department of Chemistry, University of Kentucky, Lexington, Kentucky.

* To whom correspondence should be addressed. E-mail: tom.otieno@eku.edu

properties of a three-dimensional coordination polymer of CuSCN and 2,5-dimethylpyrazine.

Experimental

2,5-Dimethylpyrazine and copper(I) thiocyanate were from commercial sources and used as received. To a slurry of CuSCN (1.00 g, 8.22 mmol) in 10 mL of acetonitrile was added 3.50 mL (32.0 mmol) of 2,5-dimethylpyrazine. The yellow precipitate that formed was isolated by filtration, washed with small amounts of acetonitrile and diethyl ether, and then dried under vacuum for 2 h. Yield, 1.35 g (94%). Anal. calculated for $C_8H_8N_4Cu_2S_2$: C, 27.34; H, 2.29; N, 15.94. Found: C, 26.43; H, 2.15; N, 15.47. IR bands (cm^{-1}): 2174 m, 2123 vs, 2078 m, 1493 vs, 1440 m, 1428 m sh, 1376 m, 1334 m, 1163 m, 1070 s, 1039 w, 970 w, 918 vw, 886 w, 768 s, 524 w, 444 m, 435 s.

Crystals for X-ray analysis were obtained by thermal gradient recrystallization as follows. A 15-cm-long test tube containing a saturated acetonitrile solution of the above yellow product over an excess of the solid was placed in a heating block such that the lower end of the tube (4.5 cm) was at about 52°C and the upper end at room temperature. Crystals were harvested after a 6-week period.

Elemental analysis was performed by Midwest Microlab, Indianapolis, IN. Infrared spectra were recorded as KBr pellets on a Bio-Rad Model FTS3000 FT-IR spectrometer. Thermogravimetric analysis (TGA) in the 30–600°C range was carried out using a TA Instruments TGA 2950 thermogravimetric analyzer. Approximately 25 mg sample was finely powdered and placed into a platinum pan and heated at a rate of 10°C/min while being purged with argon gas at a flow rate of 100 cm^3/min .

X-ray crystallographic data were collected at 173 K on a Nonius KappaCCD diffractometer. Reflections were indexed and scaled using the Denzo-SMN software package.²⁶ The structures were solved with SHELXS and refined with SHELXL from the SHELX97 program package.²⁷ All hydrogen atoms were found in difference maps

Table 1. Crystal Data and Structure Refinement

Compound	$[Cu_2(SCN)_2(2,5-me_2pyz)]_\infty$
CCDC deposit no.	188055
Color/shape	Orange/irregular block
Empirical formula	$C_8H_8Cu_2N_4S_2$
Formula weight	351.38
Temperature, K	173
Wavelength (Mo $K\alpha$), Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
	$a = 5.6850(2)$ Å
	$b = 6.9277(3)$ Å
	$c = 14.3575(6)$ Å
	$\beta = 93.435(1)^\circ$
Volume/Å ³	564.5(2)
Z	2
Density (calculated), g cm^{-3}	2.067
Absorption coefficient, mm^{-1}	4.110
$F(000)$	348
Crystal size, mm	$0.20 \times 0.12 \times 0.08$
Diffractometer	Nonius kappa CCD
θ range for data collection deg	2.84–24.99
Index ranges	$-6 \leq h \leq 6$ $-8 \leq k \leq 8$ $-17 \leq l \leq 17$
Number of reflection measured	1880
Unique data ($R_{int} = 0.0341$)	992
Absorption correction	multiscan
Max. and min. transmission	0.7346 and 0.4937
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	992/0/75
Goodness-of-fit on F^2	1.028
Final R indices [$I > 2\sigma(I)$] ^{a,b}	$R_1 = 0.0233$, $wR_2 = 0.0553$
R indices (all data) ^{a,b}	$R_1 = 0.0264$, $wR_2 = 0.0565$
Extinction coefficient, mm^{-1}	0.0063(12)
Largest diff. peak and hole, e Å ⁻³	0.344 and -0.403

$$^a R = \sum \|F_o - |F_c|\| / \sum |F_o|.$$

$$^b R_w = \left[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 \right]^{1/2}.$$

and included using suitable riding models with isotropic U tied to the corresponding heavy atom. Details of the data collection and refinement are summarized in Table 1. The atomic coordinates and isotropic displacement parameters are listed in Table 2.

Results and discussion

The copper(I) coordination environment in $[Cu_2(SCN)_2(2,5-me_2pyz)]_\infty$, **1**, is shown in

Table 2. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 \AA^2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Cu	6125(1)	1705(1)	3289(1)	16(1)
N(1)	8236(3)	569(3)	4339(1)	14(1)
C(1)	9883(4)	-727(4)	4146(2)	14(1)
C(2)	8337(4)	1318(4)	5210(2)	13(1)
C(3)	6569(4)	2806(4)	5444(2)	19(1)
S	6483(1)	-484(1)	1993(1)	15(1)
C(4)	3854(4)	-1539(4)	1892(2)	13(1)
N(2)	2038(4)	-2299(3)	1796(1)	18(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fig. 1 and selected bond lengths and angles are given in Table 3. The coordination geometry around each copper atom is made up of two sulfur atoms from two different thiocyanate ligands, one nitrogen atom from a third thiocyanate ligand, and a second nitrogen atom from a 2,5-dimethylpyrazine ligand. Bond angles about the copper atom range from $97.06(6)^\circ$ to $134.10(8)^\circ$. Thus, the CuS_2N_2 chromophore has a highly distorted tetrahedral geometry. The Cu—S bond lengths in **1**, 2.4189(8) and 2.4230(8) Å, are longer than those observed in other copper(I)-

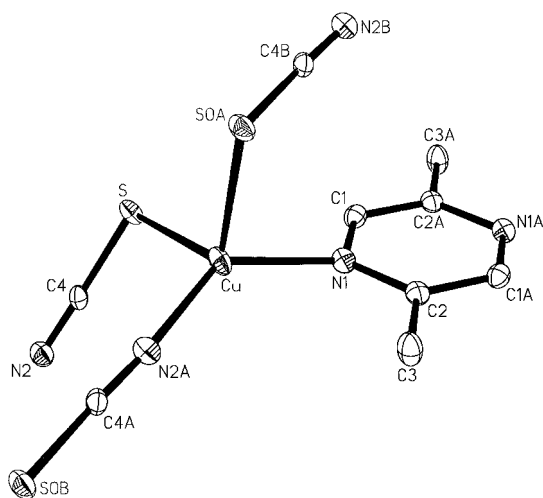


Fig. 1. A view of the copper(I) coordination environment in $[\text{Cu}_2(\text{SCN})_2(2,5\text{-me}_2\text{pyz})]_\infty$. Displacement ellipsoids are shown at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles ($^\circ$)^a

Bond lengths	
Cu—N(2)#1 ^b	1.923(2)
Cu—N(1)	2.029(2)
Cu—S	2.4189(8)
Cu—S#2 ^c	2.4230(8)
Bond angles	
N(2)#1 ^b —Cu—N(1)	134.10(8)
N(2)#1 ^b —Cu—S	107.31(7)
N(1)—Cu—S	104.78(6)
N(2)#1 ^b —Cu—S#2 ^c	103.47(7)
N(1)—Cu—S#2 ^c	97.06(6)
S—Cu—S#2 ^c	107.539(19)

^aSymmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, y + 1/2, -z + 1/2$; #2 $-x + 3/2, y + 1/2, -z + 1/2$; #3 $-x + 2, -y, -z + 1$; #4 $-x + 3/2, y - 1/2, -z + 1/2$; #5 $-x + 1/2, y - 1/2, -z + 1/2$.

^bLabeled N2A in Fig. 1.

^cLabeled SOA in Fig. 1.

pyrazine complexes, namely, $[\text{CuSCN}(2\text{-mepyz})]_\infty$ where 2-mepyz = 2-methylpyrazine (2.358(3) Å),¹¹ $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$ (2.349(2) and 2.338(2) Å),¹² and $[\text{CuSCN}(\text{pyz})]_\infty$ (2.3037(14) Å).¹³ However, Cu—S bond lengths comparable to or longer than those in **1** have been observed for other copper(I) thiocyanate complexes. For example, $[\text{Cu}(\text{SCN})(\text{quinoline})]_\infty$,²⁸ $[\text{Cu}(\text{SCN})(4\text{-methylpyrimidine})]_\infty$,¹¹ and $[\text{Cu}(\text{SCN})(\text{PCH}_3(\text{C}_6\text{H}_5)_2)_2]_2$ ²⁹ have Cu—S bond lengths of 2.407(2) Å, 2.456(1) Å, and 2.46(1) Å, respectively.

The three-dimensional structure of **1** is similar to that observed for the parent pyrazine analogue, $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]_\infty$,¹² and is shown in Fig. 2. The coordination of three thiocyanate groups (one $\mu\text{-N}$ and two $\mu\text{-S}$) about each copper atom results in the formation of ten-membered Cu—S—Cu—NCS—Cu—NCS rings. Each ring can be considered to assume a pseudo-chair conformation if the rigid rod-like thiocyanate ligand is treated as a single center. The rings are fused together to form undulating sheets perpendicular to the *c* axis. Adjacent sheets are cross-linked by 2,5-dimethylpyrazine ligands to generate a three-dimensional network containing channels running parallel to the *a* axis. Similar channels in the

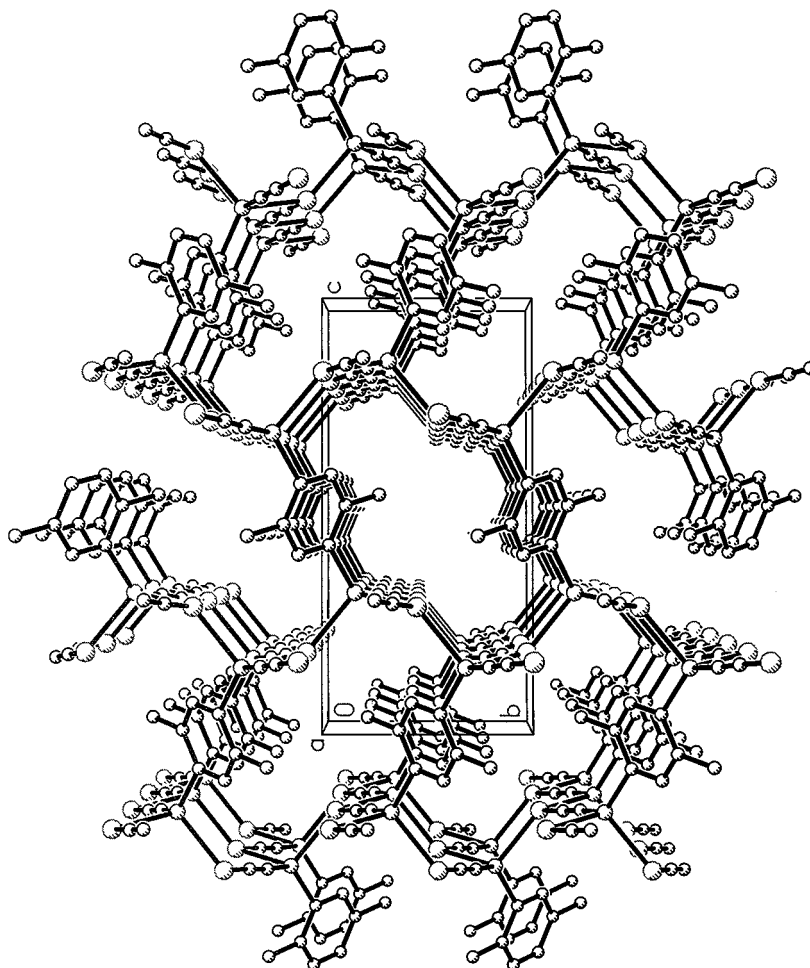


Fig. 2. A packing diagram of $[\text{Cu}_2(\text{SCN})_2(2,5\text{-me}_2\text{pyz})]_\infty$ viewed down the a axis and showing the channels. Hydrogen atoms have been omitted for clarity.

unsubstituted pyrazine analogue were found to have no solvent accessible volume.¹² Thus, the channels in **1** also would not be expected to accommodate solvent molecules, especially since the methyl substituents on the pyrazine ring impose additional steric constraints.

Compound **1** has also been characterized by infrared spectroscopy and TGA. The thiocyanate ion has three vibrational modes, namely the C–N stretching mode (ν_{CN}), the C–S stretching mode (ν_{CS}), and the NCS bending mode (δ_{NCS}). The infrared spectrum of **1** exhibits an intense band at 2123 cm^{-1} assigned to ν_{CN} . Two additional bands of weak to medium intensity (2174 cm^{-1} and

2078 cm^{-1}) are observed in the ν_{CN} stretching region. ν_{CS} and δ_{NCS} are observed at 768 cm^{-1} and 444 cm^{-1} , respectively. These spectral features are consistent with those observed for other copper(I) thiocyanate complexes.^{12,13,30} The TGA thermogram of **1** shows a weight loss corresponding to one 2,5-dimethylpyrazine in the $117\text{--}240^\circ\text{C}$ temperature range (observed = 29.6%, calculated = 30.8%). The resultant CuSCN decomposes in two steps, with weight losses of 18.2% and 6.8% observed in the temperature ranges $280\text{--}450^\circ\text{C}$ and $450\text{--}570^\circ\text{C}$, respectively. The weight of the residue observed at 570°C suggests that the product at this temperature is Cu_2S (observed = 44.5%,

calculated = 45.3%). The initial loss of the neutral ligand near 200°C has been observed for the analogous complexes, Cu₂X₂(pyz), where X = Cl, Br, or I and pyz = pyrazine.^{8,9} This is followed by the almost complete loss of the resulting metal halides in the 530–580°C temperature range.

Acknowledgments

This work was supported by Eastern Kentucky University.

References

1. Braga, D. *J. Chem. Soc., Dalton Trans.* **2000**, 3705.
2. Zaworotko, M.J. *J. Chem. Soc., Chem. Commun.* **2001**, 1.
3. Robson, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3735.
4. Hoskins, B.F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546.
5. Lever, A.B.P.; Lewis, J.; Nyholm, R.S. *Nature*, **1961**, *189*, 58.
6. Lever, A.B.P.; Lewis, J.; Nyholm, R.S. *J. Chem. Soc.* **1963**, 3156.
7. Otieno, T.; Rettig, S.J.; Thompson, R.C.; Trotter, J. *Can. J. Chem.* **1989**, *67*, 1964.
8. Persky, N.S.; Chow, J.M.; Poschmann, K.A.; Lacuesta, N.N.; Stoll, S.L.; Bott, S.G.; Obrey, S. *Inorg. Chem.* **2001**, *40*, 29.
9. Graham, M.G.; Pike, R.D.; Sabat, M.; Bailey, R.D.; Pennington, W.T. *Inorg. Chem.* **2000**, *39*, 5121.
10. Roßenbeck, B.; Sheldrick, W.S. *Z. Naturforsch., B* **2000**, *55*, 467.
11. Teichert, O.; Sheldrick, W.S. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1860.
12. Blake, A.J.; Brooks, N.R.; Champness, N.R.; Crew, M.; Hanton, L.R.; Hubberstey, P.; Parsons, S.; Shróder, M. *J. Chem. Soc., Dalton Trans.* **1999**, 2813.
13. Goher, M.A.S.; Mautner, F.A. *Polyhedron*, **1999**, *18*, 1805.
14. Goher, M.A.S.; Mautner, F.A. *J. Chem. Soc., Dalton Trans.* **1999**, 1923.
15. Siebel, E.; Ibrahim, A.M.A.; Fischer, R.D. *Inorg. Chem.* **1999**, *38*, 2530.
16. Kuhlman, R.; Schimek, G.L.; Kolis, J.W. *Polyhedron* **1999**, *18*, 1379.
17. Kawata, S.; Kitagawa, S.; Kumagai, H.; Iwabuchi, S.; Katada, M. *Inorg. Chim. Acta* **1998**, *267*, 143.
18. Begley, M.J.; Hubberstey, P.; Stroud, J. *J. Chem. Soc., Dalton Trans.* **1996**, 2323.
19. Moreno, J.M.; Suarez-Varela, J.; Colacio, E.; Avila-Rosón, J.C.; Hidalgo, M.A.; Martin-Ramos, D. *Can. J. Chem.* **1995**, *73*, 1591.
20. MacGillivray, L.R.; Subramanian, S.; Zaworotko, M.J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325.
21. Otieno, T.; Rettig, S.J.; Thompson, R.C.; Trotter, J. *Inorg. Chem.* **1993**, *32*, 1607.
22. Kitagawa, S.; Kawata, S.; Kondo, M.; Nozaka, Y.; Munakata, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3387.
23. Kitagawa, S.; Munakata, M.; Tanimura, T. *Inorg. Chem.* **1992**, *31*, 1714.
24. Turnbull, M.M.; Pon, G.; Willett, R.D. *Polyhedron*, **1991**, *10*, 1835.
25. Otieno, T.; Rettig, S.J.; Thompson, R.C.; Trotter, J. *Can. J. Chem.* **1990**, *68*, 1901.
26. Otwinowski, Z.; Minor, W. In *Methods of Enzymology: Macromolecular Crystallography, Part A*; Carter, C.W., Jr.; Sweet, R.M., Eds.; Academic Press: New York, 1997; Vol. 276, pp. 307–326.
27. Sheldrick, G.M. *SHELXS97, SHELXL97. Programs for the Solution and Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
28. Healy, P.C.; Skelton, B.W.; Waters, A.F.; White, A.H. *Aust. J. Chem.* **1991**, *44*, 1049.
29. Gaughan, A.P.; Ziolo, R.F.; Dori, Z. *Inorg. Chim. Acta*, **1970**, *4*, 640.
30. Toeniskoetter, R.H.; Solomon, S. *Inorg. Chem.* **1968**, *7*, 617.