Assembly and Crystal Structure of a Novel 1-D Coordination Polymer of Copper(II) with Thiocyanate and 4-Cyanopyridine

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A novel one-dimensional coordination polymer, *Catena*-poly [bis(4-cyano-pyridyl) copper(II)-di-thiocyanate], $^1_\infty$[Cu^{II}(cypy)$_2$($\mu_{N,S}$-SCN)$_2$] (cypy = 4-cyano-pyridyl), was synthesized in a solution reaction of Cu(NO$_3$)$_2 \cdot$3H$_2$O, 4-cyano-pyridine and KSCN in mole ratio of 1:2:2 at room temperature. Its crystal structure was determined by single-crystal X-ray diffraction. The crystal belongs to monoclinic crystal system, space group $P2_1/c$ with cell parameters $a = 1.0719(2)$, $b = 1.8441(4)$, $c = 0.9144(2)$ nm, $\beta = 110.49(3)°$ and $Z = 4$. A full-matrix least-squares refinement gave $R_1 = 0.0393$ and $wR_2 = 0.0916$ for 1554 reflections having $I > 2\sigma(I)$. The crystal is thermally stable up to approximately 170 ℃.

Keywords   coordination polymer, *catena*-poly [bis (4-cyano-pyridyl)copper(II)-di-thiocyanate], synthesis, crystal structure

Introduction

The crystal engineering of one, two, and three-dimensional coordination polymers was, in the near past years, of great interest and a rapidly developing area of research that has implications for the rational design of new functional materials.[1] This area has advanced to a stage at which it is possible to select building blocks (polydentate organic ligands) and templating species (metal atoms or ions as coordination centers) suitable for constructing desired network structures containing cavities or channels of special shape and size. Studies have shown that coordination polymers consisting of both organic and inorganic components have unusual properties in various applications.[2]

The efforts have been made in using thiocyanate ion SCN$^-$ containing N at one end and S at another end for self-assemblies of coordination polymers. Coordination polymers of some bivalent first-row transition metals with SCN$^-$ ligands have been synthesized and characterized.[3-7] Here, we report the results of synthesis and crystal structure determination of coordination polymer of copper(II) with SCN$^-$ and 4-cyano-pyridine. The 1-D coordination polymer $^1_\infty$[Cu(p-cypy)$_2$($\mu_{N,S}$-SCN)$_2$] contains two SCN$^-$ ions acting as bridging ligands and two 4-cyano-pyridine additional ligands in one unit. The coordination modes of SCN$^-$ have been discussed.

Experimental

Synthesis

All chemicals and solvents used in the synthesis were of reagent grade and without further purification.

An aqueous solution (25 mL) of Cu(NO$_3$)$_2 \cdot$3H$_2$O (0.302 g, 1.25 mmol) was slowly dripped into an acetone-water (1:2) mixed solution (50 mL) containing 4-cyano-pyridine (0.260 g, 2.5 mmol) and KSCN (0.243 g, 2.5 mmol) under stirring at room temperature. Green powders precipitated immediately. Following stirring for 30 min, the reaction solution was filtered and the filtrate was allowed to stand at 30 ℃ for evaporating

the solvents. Green column-like crystals suitable for X-ray diffraction were formed in two weeks, then isolated from the solution, washed with acetone and dried in air.

X-ray diffraction

The single crystal (0.28 mm $\times 0.22$ mm $\times 0.16$ mm) was selected for X-ray diffraction measurement. Intensity data were collected using NONIUS Kappa CCD diffractometer at $293(2)$ K, graphite-monochromated Mo K_α radiation ($\lambda = 0.071073$ nm). The total reflections of 12725 were measured, unique 2417 with $R_{int} = 0.0397$ and 1554 having $I \geqslant 2\sigma(I)$, within the limits $7.26 \leqslant 2\theta \leqslant 60.02°$.[8] The final unit cell parameters were obtained by global refinement of the positions of all collected reflections.[9] The raw data were corrected for LP factors, empirical absorption.[10] The structure was solved by direct method.[11] H atoms were added by calculated positions. All non-H atoms were refined anisotropically with full-matrix least-squares on F^2.[12] The final $R_1 = 0.0393$ and $wR_2 = 0.0916$ for 1554 reflections with $I \geqslant 2\sigma(I)$. Crystal drawings were generated by Bruke SHELXTL(V 5.1).[12]

Thermal analysis

Thermogravimetric analysis (TGA) for the title compound was performed on a RIGAGU TGA analyzer. The single-phase powder sample (7.81 mg) was loaded into alumina pan and heated in air with a ramp rate of 8 ℃/min from room temperature to 500 ℃. α-Al$_2$O$_3$ was selected as the reference.

Results and discussion

The title compound crystallizes in the monoclinic crystal system, space group $P2_1/c$. The cell parameters are $a = 1.0719(2)$, $b = 1.8441(4)$, $c = 0.9144(2)$ nm, $\beta = 110.49(3)°$, $V = 1.6931(6)$ nm^3, $Z = 4$, $\mu = 1.542$ mm^{-1}. The crystallographic data are given in Table 1. Atomic coordinates are listed in Table 2 and selected bond lengths and angles in Table 3.

The crystal structure is constructed by packing of 1-D chain $\frac{1}{\infty}[\mathrm{Cu(cypy)}_2(\mu_{N,S}\text{-}\mathrm{SCN})_2]$ running parallel to [101] direction as depicted in Fig. 1.

Table 1 Crystal data and structure refinement for $\frac{1}{\infty}[\mathrm{Cu(4\text{-}cypy)}_2(\mathrm{SCN})_2]$

Empirical formula	C$_{14}$H$_8$CuN$_6$S$_2$
Formula weight	387.92
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 1.0719(2)$ nm $\alpha = 90°$
	$b = 1.8441(4)$ nm $\beta = 110.49(3)°$
	$c = 0.9144(2)$ nm $\gamma = 90°$
Volume	1.6931(6) nm^3
Z, Calculated density	4, 1.522 mg·m^{-3}
Absorption coefficient	1.542 mm^{-1}
$F(000)$	780
Crystal size	0.28 mm $\times$ 0.22 mm $\times$ 0.16 mm
Theta range for data collection	3.63° to 30.01°
Index ranges	$-15 \leqslant h \leqslant 15$, $-25 \leqslant k \leqslant 25$, $-12 \leqslant l \leqslant 12$
Reflections collected/unique	12725/2417 ($R_{int} = 0.0397$)
Reflections with $I > 2$ sigma(I)	1554
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2417/0/212
Goodness-of-fit on F^2	0.981
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0393$, $wR_2 = 0.0916$
R indices (all data)	$R_1 = 0.0722$, $wR_2 = 0.1084$
Extinction coefficient	0.0071(16)
Largest diff. peak and hole	268 and -205 e/nm^3

Table 2 Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (nm² × 10)

	X	Y	Z	U(eq)
Cu(1)	0	0	0	40(1)
Cu(2)	5000	0	5000	46(1)
S(1)	4166(1)	1101(1)	2505(1)	62(1)
S(2)	757(1)	− 1037(1)	2692(2)	56(1)
N(1)	1703(4)	493(2)	862(4)	47(1)
N(2)	806(4)	− 705(2)	− 1181(4)	44(1)
N(3)	3229(6)	− 2530(3)	− 3852(7)	105(2)
N(4)	3344(4)	− 538(2)	4126(5)	51(1)
N(5)	4128(4)	651(2)	6216(4)	45(1)
N(6)	1759(6)	2333(3)	9218(7)	89(2)
C(1)	2724(4)	741(2)	1531(4)	39(1)
C(2)	1725(5)	− 461(2)	− 1765(5)	56(2)
C(3)	2351(5)	− 921(2)	− 2479(5)	62(2)
C(4)	2039(5)	− 1636(2)	− 2600(5)	55(1)
C(5)	1074(5)	− 1897(2)	− 2028(6)	61(2)
C(6)	503(5)	− 1396(2)	− 1306(5)	52(1)
C(7)	2703(6)	− 2146(3)	− 3295(7)	70(2)
C(8)	2281(4)	− 752(2)	3540(5)	40(1)
C(9)	2861(4)	852(2)	5565(5)	48(1)
C(10)	2226(5)	1294(2)	6305(5)	52(1)
C(11)	2955(5)	1540(2)	7785(6)	49(2)
C(12)	4265(5)	1344(3)	8468(6)	64(2)
C(13)	4816(5)	885(2)	7638(5)	57(1)
C(14)	2309(6)	1999(2)	8601(6)	63(2)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Bond lengths (nm) and angles (°)

Cu(1)—N(1)	0.1942(4)	N(1)-Cu(1)-N(1) # 1	180.0
Cu(1)—N(1) # 1	0.1942(4)	N(1)-Cu(1)-N(2) # 1	89.97(13)
Cu(1)—N(2) # 1	0.2063(2)	N(1) # 1-Cu(1)-N(2) # 1	90.03(13)
Cu(1)—N(2)	0.2063(2)	N(1)-Cu(1)-N(2)	90.03(13)
Cu(2)—N(4) # 2	0.1944(4)	N(1) # 1-Cu(1)-N(2)	89.97(13)
Cu(2)—N(4)	0.1944(4)	N(2) # 1-Cu(1)-N(2)	180.0
Cu(2)—N(5) # 2	0.2069(2)	N(4) # 2-Cu(2)-N(4)	180.0
Cu(2)—N(5)	0.2069(2)	N(4) # 2-Cu(2)-N(5) # 2	89.87(13)
Cu(1)—S(2)	0.2996(4)	N(4)-Cu(2)-N(5) # 2	90.13(13)
Cu(2)—S(1)	0.2950(4)	N(4) # 2-Cu(2)-N(5)	90.13(13)
S(1)—C(1)	0.1631(4)	N(4)-Cu(2)-N(5)	89.87(13)
S(2)—C(8)	0.1631(5)	N(5) # 2-Cu(2)-N(5)	180.0
N(1)—C(1)	0.1146(6)	C(1)-N(1)-Cu(1)	171.9(3)
N(2)—C(6)	0.1310(4)	C(1)-S(1)-Cu(2)	104.1(6)
N(2)—C(2)	0.1351(4)	C(6)-N(2)-C(2)	118.9(3)
N(3)—C(7)	0.1131(5)	C(6)-N(2)-Cu(1)	121.46(18)
N(4)—C(8)	0.1146(6)	C(2)-N(2)-Cu(1)	119.6(2)
N(5)—C(13)	0.1322(6)	C(8)-N(4)-Cu(2)	169.4(3)
N(5)—C(9)	0.1330(7)	C(8)-S(2)-Cu(1)	103.8(6)
N(6)—C(14)	0.1130(4)	N(1)-C(1)-S(1)	179.0(2)
C(2)—C(3)	0.1380(5)	N(3)-C(7)-C(4)	178.4(6)
C(3)—C(4)	0.1356(6)	N(4)-C(8)-S(2)	178.6(4)
C(4)—C(5)	0.1398(6)		
C(4)—C(7)	0.1452(5)		
C(5)—C(6)	0.1396(5)		

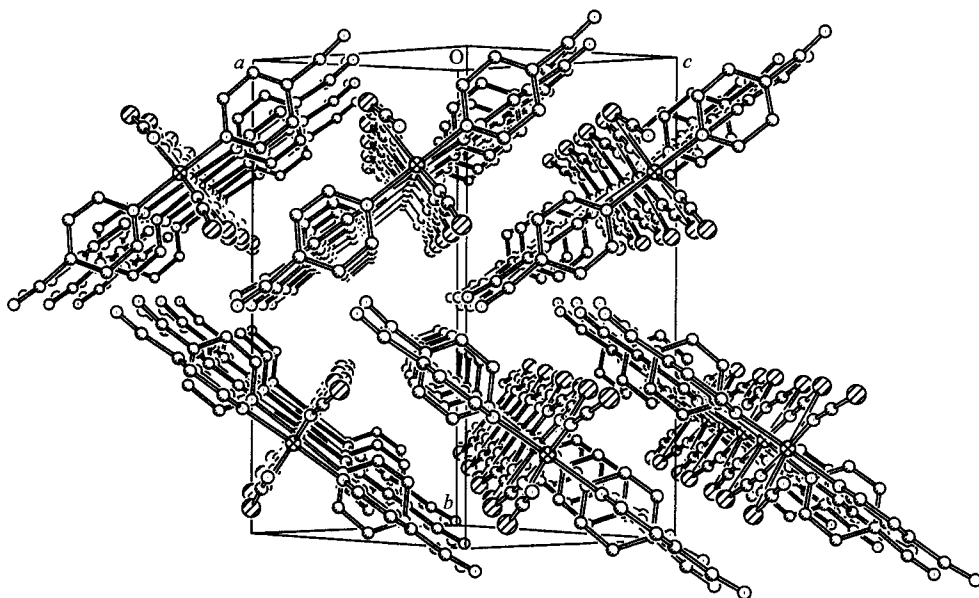Symmetry transformations used to generate equivalent atoms: # 1 − x, − y, − z; # 2 − x + 1, − y, − z + 1.

Fig. 1 A veiw of crystal structure of the title compound, including the crystallographic unit cell.

The chain contains neutral $[\,Cu\,(cypy)_2\,(\mu_{N,S}\text{-}SCN)_2\,]$ units which are linked together through two bidentate thiocyanate ligands bridging Cu(II) via N and S atoms, respectively (Fig. 2 and Fig. 3).
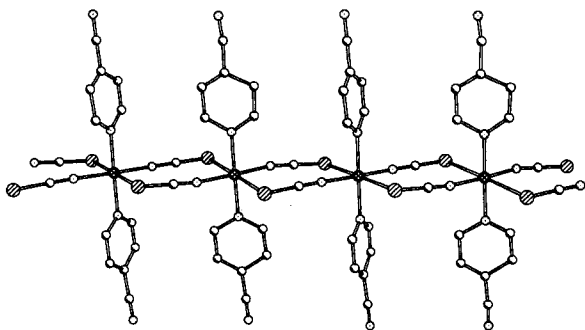

Fig. 2 Structure of the chain $\frac{1}{\infty}[\,Cu(cypy)_2(\mu_{N,S}\text{-}SCN)_2\,]$. The cross-shaded cycles are Cu(II), shaded cycles are S, open cycles are N, and the rest are C atoms, respectively.

In the chain, each Cu(II) is located in a distorted octahedron. The horizontal positions are occupied by four SCN⁻ groups, of which, two SCN⁻ groups bond Cu(II) through N—Cu bonds in a line, two link Cu(II) via S atoms in the direction perpendicular to the line. The two vertical sits are available for coordinations of pyridyl N atoms of two 4-cyano-pyridine additional ligands. The coordination octahedron is lengthened along Cu—S bonds with mean bond length of 0.2978(4)
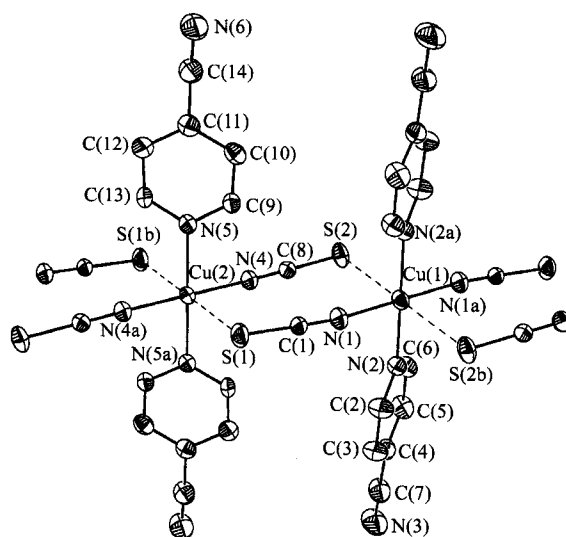

Fig. 3 Drawing of the chain unit $[\,Cu(cypy)_2(\mu_{N,S}\text{-}SCN)_2\,]$ with the atom labeling scheme.

while Cu—N bond lengths range from 0.1942(4) nm to 0.2063(2) nm. In the chain, Cu(II) ions and bridging thiocyanate groups are in the same plane. The molecular planes of all 4-cyano-pyridines are perpendicular to the plane. The molecular planes of two 4-cyano-pyridines coordinated with the same copper ion are coplanar, whereas there is a dihedral angle of about 73° between the molecular planes of two 4-cyano-pyridines coordinated with two adjacent copper ions due to intermolecular interaction.

Ligands play an important role in designing new coordination polymers for desired structures and properties. SCN^- acts, in general, as monodentate ligand in metal-thiocyanate complex molecule with N—M or S—M bond. Studies have demonstrated that the S—M bond was transformed into N—M bond at higher temperature.[13] It was shown that the complex molecule formed via N—M bond was of more stability than that via S—M bond. However, SCN^- conducts as bidentate ligand in many of the coordination polymers in which transition metal ions are bridged by thiocyanate groups through both N—M and S—M bonds in different coordination modes.[7] In $\frac{1}{\infty}[Cu(cypy)_2(\mu_{N,S}\text{-}SCN)_2]$, the bridging ligand, $\mu_{N,S}\text{-}SCN^-$, coordinates with Cu(II) to form N—Cu bond with bond angle C-N-Cu of approximately 170° and with another Cu(II) to form S—Cu with C-S-Cu of about 104°. N in SCN^- is still of stronger coordination capability than S in coordination polymers. The distance between N and Cu is about 0.1943 nm, a regular N—Cu coordination bond. While there is a weak coordination between S and Cu with the mean distance of 0.2975 nm in the coordination polymer. The feature of thiocyanate group as bidentate ligand has exhibited in the other coordination polymers mentioned above.[7] 4-cyano-pyridine as monofunctional ligand coordinates with Cu(II) only via pyridyl N atom. Coordination polymers assembled by 4-cyano-pyridine ligand would possess the structure with more dimension if the ligand was bidentate. In fact, 4-cyano-pyridine could be bifunctional bridging ligand in coordinating with transition metal ions at hydrothermal condition.[14]

The result of thermal analysis indicated that the weight loss occurred from 100—425 ℃. The sample underwent weight loss process in two steps of 100—290 ℃ and 290—425 ℃ with the minimal values of the first derivatives of the weight loss curve ($w\% - ℃$) at 170 ℃ and 360 ℃, respectively. The coordination polymer crystal should be thermal stable up to 170 ℃.

Acknowledgement

References

1   (a) Hagagrman, P. J.; Hagrman, D.; Zubeta, J. *Angew. Chem. Int. Ed.* **1999**, *38*, 2638.
    (b) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.

2   (a) Kobbel, W.; Hanack, M. *Inorg. Chem.* **1986**, *25*, 103.
    (b) Lu, J. Y.; Lawandy, M. A.; .Li, J. *Inorg. Chem.* **1999**, *38*, 2695.
    (c) Fujita, M.; Kwon, Y.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.
    (d) Miller, J. S. Epstein, A. J. *J. Chem. Soc. Commun.* **1998**, 1319.
    (e) Stang, P. J. Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.

3   Li, M.-X.; Xie, G.-Y.; Gu, Y.-D.; Chen, J.; Zheng, P.-J. *Polyhedron* **1995**, *14*, 1235.

4   (a) Moliner, N.; Real, J. A.; Munoz, M. C.; Martinez-Manez, R.; Juan, J. M. C. *J. Chem. Soc., Dalton Trans.* **1999**, 1375.
    (b) Noro, S.; Kondo, M.; Ishii, T.; Kitagawa, S.; Matsuzaka, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1569.

5   Lloret, F.; Munno, G. D.; Julve, M.; Cano, J.; Ruiz, R.; Caneschi, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 135.

6   (a) Monfort, M.; Ribas, J.; Solans, X. *Inorg. Chem.* **1994**, *33*, 4271.
    (b) Vicente, R.; Escuer, A.; Ribas, J. *J. Chem. Soc., Dalton Trans.* **1994**, 259.

7   (a) Navarro, J. A. R.; Romero, M. A.; Salas, J. M.; Quiros, M.; Tiekink, E. R. T. *Inorg. Chem.* **1997**, *36*, 4988.
    (b) Diaz, C,; Ribas, J.; Sans, N.; Solans, X.; Font-Bardia, M. *Inorg. Chim. Acta* **1999**, *286*, 169.

8   Nonius, B. V., *Collect*, data collection software, Deft, Netherlands, **1998**.

9   Otwinowski, Z.; Minor, W. *Method in Enzymology*, Vol. 276: Eds.: Cater, Jr. C. W.; Sweet, R. M., Academic Press, London, **1997**, Part A, pp. 307—326.

10 Mackay, S.; Gilmore, C. J.; Edwards, C.; Tremayne, M.; Stuart, N.; Shankland, K., *maXus*, a computer program for the solution and refinement of crystal structures from diffraction data, University of Glasgow, Scotland UK, Nonius, B. V., Delft, The Netherlands and MacScience Co. Ltd., Yomahama, Japan, **1998**.

11 Sheldrick, G. M. *SHELX-97*, PC Version, University of Goettingen, Germany, **1997**.

12 Sheldrick, G. M. *SHELXTL*, Version 5.1, Bruke Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1998**.

13 Basolo, F.; Burmeister, J. L.; Poe, A. J. *J. Amer. Chem. Soc.* **1963**, *85*, 1700.

14 Evansad, O. R.; Lin, W. *Inorg. Chem.* **2000**, *39*, 2189.