Synthesis and Structure of a Novel Copper(II) Thiocyanate Complex with 4-(Dimethylamino)pyridine and *N,N*-Dimethylformamide

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A novel copper(II) thiocyanate complex with 4-(dimethylamino)pyridine (DMAP) and *N,N*-dimethylformamide (DMF), $[\text{Cu}(\text{DMAP})_2(\text{SCN})_2(\text{DMF})_2]$, was synthesized. The title complex was crystallized in the triclinic system, space group $P\bar{1}$ with $a = 8.476(1)\text{\AA}$, $b = 9.404(1)\text{\AA}$, $c = 9.924(1)\text{\AA}$, $\alpha = 91.186(2)^\circ$, $\beta = 113.989(3)^\circ$, $\gamma = 103.543(2)^\circ$, $V = 696.6(2)\text{\AA}^3$ and $Z = 1$. In the title complex, the Cu(II) atom is placed in a centrosymmetric octahedral environment. The molecules are linked by two kinds of weak hydrogen-bonds, C-H...O and C-H...S, generating an extended two-dimensional supramolecular network structure in the *ab* plane.

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Inorganic-organic hybrid materials constructed by a self-assembly process have been developed at a tremendous rate recently because of their expansion by potential magnetic, optical, electronic and catalytic applications.¹ We have been interested in employing a self-assembly strategy using small and simple molecules such as azide and thiocyanate for supramolecular complexes, and to explore the relationship between the structure and the magnetic properties. In recent years, it has been found that weak hydrogen-bonds (C-H...X, X = O, N, Cl, Br, S) play important roles in molecular self-assembly into crystal structures, and affect the crystal symmetry.² As one part of our systematic work, herein we report on the synthesis and crystal structure of the copper(II) thiocyanate complex with 4-(dimethylamino)pyridine and *N,N*-dimethylformamide.

A methanolic solution (10 ml) of 4-(dimethylamino)pyridine (0.24 g 2 mmol) was added to a methanolic solution (10 ml) of a $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.303 g, 1 mmol). The solution was stirred for 15 min at room temperature. Then, a methanolic solution (10 ml) of NH_4SCN (0.152 g, 2 mmol) was added dropwise to this solution with constant stirring. After 30 min of extra stirring, the precipitate was filtered and dissolved in plentiful *N,N*-dimethylformamide and then filtered. The filtrate was allowed to stand at room temperature for slow evaporation. After one

month, green block-shaped crystals (Fig. 1) suitable for X-ray diffraction were obtained from the solution.

A green single crystal with dimensions of $0.37\text{ mm} \times 0.34\text{ mm} \times 0.28\text{ mm}$ was selected for X-ray diffraction analysis. Data collection was performed on a BRUKER SMART 1000 CCD diffract meter using Mo K_α radiation ($\lambda = 0.71073\text{ \AA}$). The structure was solved by a direct-methods program and expanded with a difference Fourier technique.³ The non-hydrogen atoms were refined with SHELX-97⁴ anisotropically by the full-matrix least-squares method based on F^2 with all observed reflections. The hydrogen atoms were generated geometrically with

Table 1 Crystal and experimental data

Empirical formula	$\text{C}_{22}\text{H}_{34}\text{CuN}_8\text{O}_2\text{S}_2$
Formula weight	570.23
Temperature	298 K
Wavelength	0.71073
Crystal system/Space group	triclinic, $P\bar{1}$
Unit cell dimensions	$a = 8.4760(10)\text{\AA}$, $\alpha = 91.186(2)^\circ$ $b = 9.4040(12)\text{\AA}$, $\beta = 113.989(3)^\circ$ $c = 9.9240(13)\text{\AA}$, $\gamma = 103.543(2)^\circ$
Volume	$696.60(15)\text{\AA}^3$
Z	1
Density (calculated)	1.359 Mg/m^3
Absorption coefficient	0.968
$F(0\ 0\ 0)$	299
Crystal size	$0.37\text{ mm} \times 0.34\text{ mm} \times 0.28\text{ mm}$
θ range for data collection [$^\circ$]	2.25 to 25.01
Index ranges	$-10 < h < 7$, $-10 < k < 11$, $-11 < l < 11$
Reflections collected/unique	3614/2406
Absorption correction	multi-scan
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2406/0/164
Goodness-of-fit on F^2	1.091
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0318$, $wR = 0.0785$
R indices (all data)	$R1 = 0.0403$, $wR = 0.0846$
Largest diff. peak and hole	0.193 and $-0.343\text{ e.\AA}^{-3}$

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Fig. 1 Chemical structure of the title complex.

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Table 2 Atomic coordinates ($\text{\AA} \times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U(eq)
Cu(1)	0	5000	5000	42(1)
N(1)	1852(3)	6428(2)	4574(2)	41(1)
N(2)	5564(3)	9124(2)	3314(2)	47(1)
N(3)	273(3)	3360(2)	3891(2)	46(1)
N(4)	2707(3)	4415(3)	9789(2)	55(1)
O(1)	2465(3)	4558(2)	7438(2)	60(1)
S(1)	271(1)	1286(1)	1597(1)	65(1)
C(1)	1458(3)	7503(3)	3722(3)	46(1)
C(2)	2622(3)	8410(3)	3289(3)	45(1)
C(3)	4382(3)	8289(2)	3752(2)	38(1)
C(4)	4810(3)	7200(3)	4698(3)	42(1)
C(5)	3540(3)	6319(3)	5040(3)	43(1)
C(6)	7403(3)	9014(3)	3887(3)	57(1)
C(7)	5074(4)	10194(3)	2288(3)	63(1)
C(8)	46(3)	2504(3)	2941(3)	40(1)
C(9)	2475(4)	5067(3)	8589(3)	54(1)
C(10)	2709(6)	5112(4)	11105(4)	91(1)
C(11)	3019(5)	2954(3)	9854(4)	74(1)

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

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

Cu(1)-N(3)	1.987(2)	Cu(1)-N(1)	2.0057(19)	O(1)-C(9)	1.225(3)
Cu(1)-O(1)	2.5943(18)	Cu(1)-N(1) ^{eq}	2.0057(19)	C(9)-N(4)	1.315(3)
Cu(1)-O(1) ^{eq}	2.5943(18)	N(3)-C(8)	1.150(3)	N(4)-C(10)	1.449(4)
Cu(1)-N(3) ^{eq}	1.987(2)	C(8)-S(1)	1.632(3)	N(4)-C(11)	1.456(4)
O(1)-Cu(1)-N(3)	90.17(7)	N(3)-Cu(1)-N(3) ^{eq}	180.00(1)	Cu(1)-N(1)-C(5)	122.24(16)
N(3)-Cu(1)-O(1) ^{eq}	89.83(7)	O(1)-Cu(1)-O(1) ^{eq}	180.00	Cu(1)-O(1)-C(9)	115.24(17)
N(3)-Cu(1)-N(1)	89.84(8)	N(1)-Cu(1)-N(1) ^{eq}	180.00(9)	O(1)-C(9)-N(4)	126.3(3)
N(3)-Cu(1)-N(1) ^{eq}	90.16(8)	N(3)-C(8)-S(1)	179.8(3)	Cu-Cu	9.404
N(1)-Cu(1)-O(1)	90.68(7)	Cu(1)-N(3)-C(8)	161.2(2)		
N(1) ^{eq} -Cu(1)-O(1)	89.32(7)	Cu(1)-N(1)-C(1)	122.20(16)		

Symmetry transformation used to generate the equivalent atoms: #1: $-x, -y+1, -z+1$.

isotropic thermal parameters. The experimental conditions, crystal data and structure refinement results are summarized in Table 1. The final positional parameters for non-hydrogen atoms are given in Table 2, and the selected bond lengths and angles are listed in Table 3. The hydrogen-bonding distances and angles are presented in Table 4. A view of an ORTEP plot of the title complex is shown in Fig. 2.

The structure of the title complex is made up of neutral $[\text{Cu}(\text{DMAP})_2(\text{SCN})_2(\text{DMF})_2]$ units (Fig. 2). The copper is in a elongated octahedral environment with four short Cu-N (DMAP and SCN) bonds [1.987(2) – 2.0057(19)] in the equatorial plane and two long axial Cu-O(DMF) bonds [2.5943(18) $\text{\AA}$]. All of the bond angles of N-Cu(1)-N are exactly 180.00° which is equal with the angles of O-Cu(1)-O (180.00°), showing their linear coordination. The thiocyanate ions are quasi-linear with the same SCN angles being $179.8(3)$. The shortest intermolecular metal-metal separation is $9.404 \text{ \AA}$, which is slightly longer than the literature value ($7.769 \text{ \AA}$) of a similar structural complex, $[\text{Co}(\text{pyd})_4(\text{SCN})_2]$.⁵ The hydrogen-bonds play important roles in the crystal packing of the title

Fig. 2 ORTEP plot of the title complex. The thermal ellipsoid for the image represent a 50% probability limit.

Fig. 3 Two-dimensional network structure of the title complex linked by weak hydrogen bonds.

compound. The one-dimension chain is linked by weak hydrogen-bonds formed by *methyl* hydrogen atoms bonded to thiocyanate sulfur atoms (C(6)-H(6B)···S(1)). A one-dimension chain is extended into two-dimension supramolecular network by another intermolecular hydrogen-bonds, which are formed by *methyl* hydrogen atoms with oxygen atoms of *N,N*-dimethylformamide (C(6)-H(6A)···O(1)) (Fig. 3). Further details about the crystal-structure investigation are available free of charge at www.ccdc.ac.uk/conts/retrieving.html or deposit@ccdc.cam.ac.uk.

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