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Crystal structure of poly[bis(μ_2 -2,6-bis(1-imidazoly)pyridine- $\kappa^2 N, N'$)-bis(thiocyanato- $\kappa^1 N$)copper(II)] dithiocyanate, $C_{24}H_{18}CuN_{12}S_2$

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Abstract

$C_{24}H_{18}CuN_{12}S_2$, monoclinic, $P2_1/c$ (no. 4), $a = 11.038(2)$ Å, $b = 8.9312(18)$ Å, $c = 16.083(5)$ Å, $\beta = 125.66(2)^\circ$, $V = 1288.2(6)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0265$, $wR_{ref}(F^2) = 0.0974$, $T = 293$ K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of materials

All the reagents were commercially available and used as received without further purification. About 13.5 mg CuSCN (0.1 mmol) and 10.3 mg NH_4SCN (0.1 mmol) were dissolved in DMF (3 mL) with strong stirring to obtain a colorless solution. Then, 42.2 mg 2,6-bis(1-imidazoly)pyridine (2,6-BIP) (0.2 mmol) was added to the mixture, which turns into the blue-green solution immediately. After filtration, 1 mL DMF and 5 mL acetonitrile were added to the upper layer of the filtrate as buffer solution and diffusion solution, sequentially. Green crystals were obtained after a week at room temperature in the dark with a yield of 38 mg (64% based Cu). Anal. Calcd. for $C_{24}H_{18}CuN_{12}S_2$: C, 47.87%; H, 3.01%; N, 27.91%. Found C, 48.02%; H, 3.03%; N, 27.76%. IR (KBr, ν/cm^{-1}): 2083(s), 2054(s), 1654(m), 1605(s), 1585(m),

Table 1: Data collection and handling.

Crystal:	Block, red
Size:	0.18 × 0.15 × 0.12 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.05 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	26°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6033, 2496, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2082
$N(\text{param})_{\text{refined}}$:	179
Programs:	Bruker programs [1], OLEX2 [2], SHELX [3, 4], PLATON [5]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cu1	0.0000	0.0000	0.0000	0.03267 (18)
S1	−0.32137 (14)	−0.04437 (13)	−0.37442 (7)	0.0776 (4)
N1	0.2056 (2)	0.4126 (2)	0.12582 (16)	0.0324 (5)
N2	0.0776 (2)	0.2157 (2)	0.03442 (17)	0.0361 (5)
N3	0.2557 (2)	0.5153 (2)	0.27563 (17)	0.0311 (5)
N4	−0.1542 (3)	0.0728 (3)	−0.1783 (2)	0.0544 (7)
N6	0.2931 (2)	0.6057 (2)	0.42386 (16)	0.0335 (5)
C1	0.1392 (3)	0.2831 (3)	0.1231 (2)	0.0329 (6)
H1	0.1375	0.2469	0.1766	0.039*
C2	0.1035 (3)	0.3070 (3)	−0.0227 (2)	0.0416 (7)
H2	0.0709	0.2881	−0.0896	0.050*
C3	0.1829 (3)	0.4270 (3)	0.0325 (2)	0.0414 (7)
H3	0.2160	0.5045	0.0118	0.050*
C4	0.2990 (3)	0.5035 (3)	0.2145 (2)	0.0300 (6)
C5	0.4265 (3)	0.5661 (3)	0.2326 (2)	0.0378 (6)
H5	0.4539	0.5513	0.1884	0.045*
N5	0.1602 (2)	0.5600 (2)	0.48272 (17)	0.0341 (5)
C6	0.5110 (3)	0.6518 (3)	0.3199 (2)	0.0436 (7)
H6	0.5972	0.6978	0.3348	0.052*
C7	0.4700 (3)	0.6703 (3)	0.3851 (2)	0.0403 (7)
H7	0.5256	0.7288	0.4438	0.048*
C8	0.3416 (3)	0.5973 (3)	0.3591 (2)	0.0322 (6)
C12	−0.2225 (3)	0.0252 (3)	−0.2593 (2)	0.0395 (7)
C11	0.1728 (3)	0.5339 (3)	0.4079 (2)	0.0363 (6)
H11	0.1080	0.4741	0.3514	0.044*
C9	0.3593 (3)	0.6829 (3)	0.5149 (2)	0.0432 (7)
H9	0.4438	0.7430	0.5459	0.052*
C10	0.2767 (3)	0.6533 (3)	0.5499 (2)	0.0416 (7)
H10	0.2956	0.6905	0.6104	0.050*

1491(s), 1458(s), 1319(w), 1286(w), 1233(m), 1176(w), 1061(m), 1004(w) (pyridine: C=N), 849(w), 792(m), 743(w), 653(m).

Experimental details

The structure was solved by direct methods and refined using the SHELX software [3]. All of the hydrogen atoms were added using a riding model [4].

Comment

Coordination polymers (CPs) have received enormous interests because of their intriguing skeletal structures, as well as the potential applications in gas absorption [6], catalysis [7], magnetism [8, 9], photoluminescence [10–12] and so on. Consequently, considerable efforts in this field have been devoted to the design and syntheses of various kinds of CPs to obtain desirable properties [13]. To extend the types of CPs, different rigid or flexible ligands have been extensively used in the preparation of CPs [14, 15]. In recent years, many CPs based on semi-rigid ligands such as bis(imidazole) derivatives have been reported [16, 17]. From the view of structural chemistry, the hinged 2,6-BIP molecule is a typical semi-rigid ligand, in which the C–N bonds between three rings can rotate to some extent. Therefore, the introduction of 2,6-BIP ligand can affect the spatial configuration of CPs and then modify the corresponding properties.

As shown in the upper part of the figure, the asymmetric unit of the title structure consists of a half Cu(II) cation (located on a center of symmetry), one 2,6-BIP molecule and one SCN[−] ion. The Cu(II) center is six-coordinated by six N atoms, in which two N atoms from SCN[−] ions and four from 2,6-BIP ligands, forming an octahedral configuration. The Cu–N bond lengths are in the range of 2.016(2)–2.419(3) Å, while the bond angles of N–Cu–N range from 87.80(9) to 180.0°. The connection between Cu(II) ions and 2,6-BIP ligands leads to a four-membered metal ring, and these rings are further extend to a two-dimensional network, exhibiting a four-connected sql topological structure (lower part of the figure). Due to the rotability of C–N bond in 2,6-BIP ligand, the dihedral angles between the pyridine ring and two imidazole rings are 3.4° and 35.6°, respectively, which resulting in the 2D structure of title CP to be helical.

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