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NOTE

Synthesis and Crystal Structure of 4,4'-Di-2-pyridyl-2,2'-dithiodipyrimidine ($C_{18}H_{12}N_6S_2$)

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A new heterocylic sulfide ligand with molecular formula $C_{18}H_{12}N_6S_2$, named as 4,4'-di-2-pyridyl-2,2'-dithiodipyrimidine, was formed by the reaction of 4-pyridin-2-yl-pyrimidine-2-thiol with ferric nitrate. The crystal is monoclinic, space group $P2_1/c$ with unit cell parameters: a = 11.777 (2) Å, b = 7.2830 (15) Å, c = 20.182 (4) Å, $\alpha = 90°$, $\beta = 98.832$ (4)°, $\gamma = 90°$, V = 1710.5 (6) Å^3, Z = 4, Mr = 376.47, Dc = 1.470 g/cm^3, $\mu = 0.327$ mm^{-1}, F(000) = 776, R = 0.0378, wR = 0.0749 for 1820 reflections with $I > 2\sigma(I)$.

Key Words: 4-Pyridin-2-yl-pyrimidine-2-thiol, Hydrogen bonds, Heterocylic sulfide.

There has been increasing interest of heterocylic sulfide ligands in the field of coordination chemistry[1-6]. In our previous paper, we reported two disulfide ligands derived from 4-pyridin-pyrimidine-2-thiol[5,6]. Herein reported is a new disulfide complex $C_{18}H_{12}N_6S_2$.

All reagents for synthesis were commercially available and employed as received or purified by standard methods prior to use. 4-Pyridin-2-yl-pyrimidine-2-thiol was prepared by general procedure reported in the literature[7]. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer.

Synthesis: $Fe(NO_3)_3 \cdot 9H_2O$ metal salt (0.1 mmol) was mixed with 4-pyridin-pyrimidine-2-thiol (0.1 mmol) and NaOH (0.1 mmol) in 20 mL of CH_3CN. The reaction mixture was stirred for 1 h and then filtered. The purple mother solution was allowed for one week to evaporate slowly and obtained colorless crystals block-shaped single crystals 1 suitable for X-ray analysis. Yield 57.1 %. Anal. calcd. for $C_{18}H_{12}N_6S_2$: C, 57.43; H, 3.21; N, 22.32 %. Found: C, 57.49; H, 3.30; N, 22.17.

Crystal structure determination: A single crystal of compound with dimensions of 0.2 mm × 0.2 mm × 0.2 mm was selected for crystallographic data collection at 291(2)K and structure determination on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). A total of 8261 reflections were collected in the range of $2° \le q \le 25°$, of which 3009 reflections

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were unique with $R_{int} = 0.055$. The data were collected using SMART and reduced by the program SAINT. All the structures were solved by direct methods and refined by full-matrix least squares method on F^2_{obs} by using SHELXTL-PC software package. Non-hydrogen atoms were placed in geometrically calculated positions. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 235 variable parameters for 3009 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.0378 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.0749 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.0280P)^2]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are are corresponding to 0.15 and -0.19 e/Å^3, respectively.

The selected bond lengths and bond angles in Table-1. Respecting, Fig. 1 shows the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound. In Fig. 1, the C-S-S-C torsion angle of 82.72 (9)° is similar with that in its analogue, namely 2,2'-dithiobis(4-pyridin-3-yl-pyrimidine)[5]. The S-S bond length of 2.0113 (9) Å in Fig. 1 is within the normal range[1,2,5,6]. It is noted that the pyrimidinyl ring and the pyridyl ring of title complex are obviously not coplanar, the dihedral angles between the two heterocyclic rings is *ca*. 4.0° or 11.1°. In crystal packing, it is interesting to observe that the C-H···N intermolecular hydrogen bonds are formed between adjacent molecules resulting in a 3D supramolecular framework.

TABLE-1
SELECTED BOND DISTANCES (Å) AND ANGLES (º)

S1-S2	2.0113 (9)	N3-C5	1.343 (3)	N4-C13-N5	128.6 (2)
S1 -C13	1.7690 (2)	N3 -C9	1.329 (3)	N6-C14-C10	115.7 (2)
S2 -C4	1.7830 (2)	S2-S1-C13	104.63 (8)	N6-C14-C19	122.9 (2)
N1 -C1	1.3430 (3)	S1-S2-C4	105.66 (8)	S1-C13-N5	120.23 (17)
N1-C4	1.3280 (3)	C1-N1-C4	115.37 (19)	S1-C13-N4	111.17 (15)
N2-C3	1.3380 (3)	C3-N2 -C4	113.6 (2)	C5-N3-C9	116.5 (2)
N2-C4	1.3140 (3)	–	–	–	–

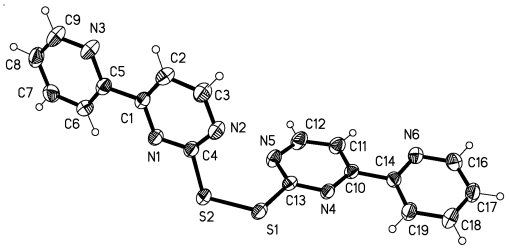

Fig. 1. Molecular structure of the present compound

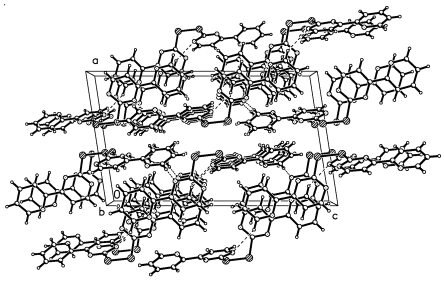

Fig. 2. View of a 3D supramolecular framework of present compound showing the intermolecular hydrogen bonding

TABLE-2
HYDROGEN BOND DISTANCES (Å) AND ANGLES (º)

Type (D-H…A)	d(D-H)	d(H…A)	∠(DHA)	d(D…A)	A
C9-H9…N5	0.9300	2.6100	149.00	3.437(3)	-x, -1/2 + y,3/2-z
C16-H16…N1	0.9300	2.5900	174.00	3.521(3)	x, 5/2-y, ½ + z

Conclusion

Crystal structure of a new heterocylic disulfide complex has been synthesized and characterized byelemental analysis and X-ray diffraction analysis.

Supplementary material

Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 705137.

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