Crystal structure of bis(isocyanato-κ^1N)-bis(2-(pyridin-4-ylthio)pyrazine-κ^1N) zinc(II), $C_{20}H_{14}N_8S_4Zn$

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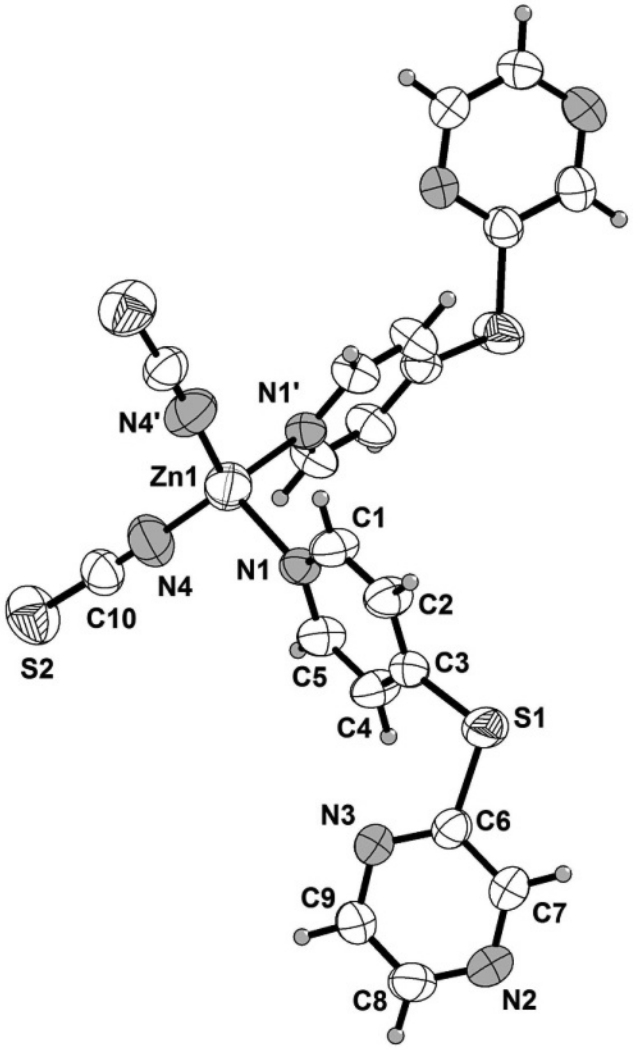

Abstract

$C_{20}H_{14}N_8S_4Zn$, monoclinic, *C*2/*c* (no. 15), a = 26.041(3) Å, b = 5.7001(6) Å, c = 16.676(2) Å, β = 100.773(7)°, V = 2431.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.0380, $wR_{ref}(F^2)$ = 0.1115, T = 296 K.

Source of material

All reagents and solvents from commercial sources were used without further purification. With the sodium pyridine-4-thiolate (0.67 g, 5 mmol) and 2-chloropyrazine (0.6 g, 5.2 mmol), 4-pyridyl-2-pyrazinyl sulfide was obtained through the synthetic procedure reported in [1]. $Zn(NCS)_2$ (18.1 mg, 0.1 mmol) and 2-(pyridine-4-ylthio)pyrazine (19 mg, 0.1 mmol) were dissolved in 1 ml methanol followed by the addition of 3 mL of mixed solvent of methanol and acetonitrile, then stirred at room temperature for 3 hours. The colourless solution was filtered and left to stand in air to slowly evaporate the solvent. Colourless block-shaped crystals of the title compound suitable for X-ray diffraction were deposited after a week. 12.6 g, 45% yield.

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Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.2×0.3×0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.79 cm^{-1}
Diffractometer, scan mode:	Bruker Smart APEXII CCD, φ and ω
$2\theta_{max}$:	56.37°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8991, 2854
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1945
$N(param)_{refined}$:	150
Programs:	SHELX [6], DIAMOND [7]

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses. The U_{iso} values of the hydrogen atoms of methyl groups were set to $1.5U_{eq}$(C) and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{eq}$(C, N).

Discussion

The semi-rigid dipyridyl sulfide and its N-positional isomers are totally different from the linear 4,4'-bipyridine ligand, as they show more flexible coordination modes in coordination supramolecular assembly on account of the rotatable C(sp2)–S bonds and the variable C(sp2)–S–C(sp2) angle [2]. So far, the coordination supramolecular architectures of various isomeric dipyridyl sulfide ligands have been reported [3]. But, studies dealing with the unsymmetrically bent-shaped ligands containing pyridyl and pyrazinyl moieties are rare [1, 4]. Herein, we report the structure of a complex with the unsymmetrical bent-shaped ligand 2-(pyridine-4-ylthio)pyrazine, a multidentate ligand bearing a C(sp2)–S–C(sp2) fragment. In the mononuclear complex, each zinc(II) center is surrounded by two N atoms from two independent 2-(pyridine-4-ylthio)pyrazine ligands (Zn1–N1 = 2.032(19) Å) and two independent isocyanato ligands (Zn1–N4 = 1.912(3) Å). Each 2-(pyridine-4-ylthio)pyrazine ligand exhibits a terminal ligand with one pyridine nitrogen atom linking to one zinc(II) atom, which combines the a pair of isocyanato anions to yield a the mononuclear complex (Fig.). Herein, the C3–S1–C6 angles of the 2-(pyridine-4-ylthio)pyrazine is 103.47(11)°. Along the *b* direction, the mononuclear units are arranged and stacked to form an infinite one-dimensional column motif, which form contacts with adjacent ones through S(isocyanato)···π(pyrazine ring) = 3.711(3) Å) interactions [5].

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	8*f*	0.5990	1.0813	0.2203	0.077
H(2A)	8*f*	0.6599	0.8082	0.2756	0.079
H(4A)	8*f*	0.5836	0.7310	0.4608	0.078
H(5A)	8*f*	0.5260	1.0105	0.4021	0.073
H(7A)	8*f*	0.7057	0.2179	0.5412	0.082
H(8A)	8*f*	0.7215	0.6086	0.7345	0.087
H(9A)	8*f*	0.6915	0.9207	0.6558	0.089

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	½	1.29600(7)	¼	0.0558(3)	0.0505(2)	0.0580(3)	0	–0.0025(2)	0
S(1)	8*f*	0.67363(3)	0.5128(1)	0.41036(4)	0.0963(6)	0.0768(5)	0.0543(5)	0.0368(4)	0.0055(4)	–0.0008(3)
S(2)	8*f*	0.42825(5)	1.7349(2)	0.43795(7)	0.1072(8)	0.1011(7)	0.0962(7)	–0.0003(5)	0.0458(6)	–0.0174(5)
N(1)	8*f*	0.55659(8)	1.0742(3)	0.3061(1)	0.048(1)	0.055(1)	0.045(1)	–0.0007(9)	0.0016(9)	–0.0004(9)
N(2)	8*f*	0.7167(1)	0.3792(4)	0.6467(2)	0.101(2)	0.065(1)	0.064(2)	0.011(1)	–0.003(1)	0.013(1)
N(3)	8*f*	0.6833(1)	0.7657(4)	0.5493(1)	0.091(2)	0.049(1)	0.057(2)	0.000(1)	0.002(1)	0.004(1)
N(4)	8*f*	0.4700(1)	1.4660(4)	0.3286(2)	0.082(2)	0.077(2)	0.085(2)	0.009(2)	0.004(1)	–0.022(1)
C(1)	8*f*	0.5961(1)	1.0111(5)	0.2697(2)	0.068(2)	0.078(2)	0.049(2)	0.012(2)	0.014(1)	0.012(1)
C(2)	8*f*	0.6327(1)	0.8467(5)	0.3024(2)	0.065(2)	0.082(2)	0.054(2)	0.018(2)	0.019(1)	0.008(1)
C(3)	8*f*	0.6289(1)	0.7399(4)	0.3747(2)	0.059(2)	0.054(1)	0.044(1)	0.006(1)	–0.000(1)	–0.002(1)
C(4)	8*f*	0.5878(1)	0.8016(5)	0.4121(2)	0.066(2)	0.079(2)	0.050(2)	0.011(1)	0.013(1)	0.016(1)
C(5)	8*f*	0.5533(1)	0.9685(5)	0.3762(2)	0.054(2)	0.077(2)	0.052(2)	0.008(1)	0.010(1)	0.005(1)
C(6)	8*f*	0.68717(9)	0.5556(4)	0.5178(2)	0.050(2)	0.051(1)	0.056(2)	0.003(1)	0.006(1)	0.005(1)
C(7)	8*f*	0.7037(1)	0.3630(5)	0.5659(2)	0.085(2)	0.052(1)	0.065(2)	0.013(1)	0.007(2)	0.005(1)
C(8)	8*f*	0.7125(1)	0.5891(5)	0.6783(2)	0.086(2)	0.072(2)	0.052(2)	–0.010(2)	–0.005(2)	0.004(1)
C(9)	8*f*	0.6952(1)	0.7777(5)	0.6306(2)	0.106(3)	0.052(1)	0.059(2)	–0.010(2)	0.003(2)	–0.004(1)
C(10)	8*f*	0.4522(1)	1.5753(5)	0.3749(2)	0.065(2)	0.061(2)	0.070(2)	–0.006(1)	0.004(2)	–0.008(1)

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