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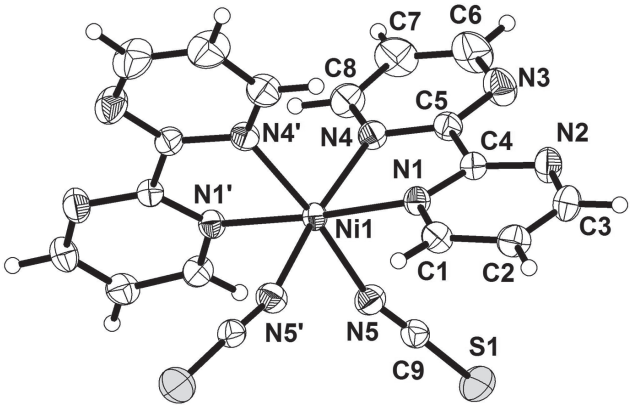
Kwang Ha*

Crystal structure of *cis*-bis(2,2′-bipyrimidine-κ^{2}N, N′)bis(thiocyanato-κ*N*)nickel(II), $C_{18}H_{12}N_{10}NiS_2$



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Abstract

$C_{18}H_{12}N_{10}NiS_2$, tetragonal, $I4_1/a$ (no. 88), $a = 12.1303(5)$ Å, $c = 28.7471(12)$ Å, $V = 4230.0(4)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0329$, $wR_{ref}(F^2) = 0.0854$, $T = 223(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a solution of $Ni(SCN)_2{\cdot}4H_2O$ (0.084 g, 0.34 mmol) in MeOH (10 mL) was added 2,2′-bipyrimidine (bpym; 0.108 g, 0.683 mmol) and stirred for 10 min at 50 °C. The formed precipitate was separated by filtration, washed with MeOH and ether and dried at room temperature, to give a yellow powder (0.0747 g). Crystals were obtained by slow evaporation from an *N*,*N*-dimethylformamide solution at 60 °C.

Table 1: Data collection and handling.

Crystal:	Yellow block Size 0.20 × 0.12 × 0.08 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	11.4 cm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
$2\theta_{max}$, completeness:	56.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	84487, 2635, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2250
$N(param)_{refined}$:	141
Programs:	Bruker programs [9], SHELX [10], ORTEP-3 [11], PLATON [12]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.2500	0.08549(2)	0.02397(10)
S1	0.18497(5)	0.27959(6)	−0.01505(2)	0.05311(18)
N1	0.48201(12)	0.41965(12)	0.08796(5)	0.0261(3)
N2	0.34557(14)	0.55420(14)	0.10439(6)	0.0370(4)
N3	0.23769(15)	0.39851(16)	0.15792(7)	0.0440(4)
N4	0.37278(13)	0.26797(12)	0.13417(5)	0.0281(3)
N5	0.37660(13)	0.24483(13)	0.03621(6)	0.0333(3)
C1	0.53861(16)	0.49300(15)	0.06289(7)	0.0318(4)
H1	0.6062	0.4725	0.0494	0.038*
C2	0.49911(18)	0.59865(16)	0.05651(7)	0.0366(4)
H2	0.5371	0.6503	0.0381	0.044*
C3	0.40206(19)	0.62486(16)	0.07814(7)	0.0396(5)
H3	0.3738	0.6964	0.0743	0.047*
C4	0.38812(14)	0.45409(14)	0.10792(6)	0.0269(3)
C5	0.32795(15)	0.36888(15)	0.13538(6)	0.0288(4)
C6	0.1886(2)	0.3175(2)	0.18221(10)	0.0549(6)
H6	0.1242	0.3342	0.1990	0.066*
C7	0.2281(2)	0.2120(2)	0.18358(9)	0.0523(6)
H7	0.1928	0.1571	0.2012	0.063*
C8	0.32110(18)	0.18927(17)	0.15825(7)	0.0391(5)
H8	0.3490	0.1170	0.1578	0.047*
C9	0.29653(16)	0.25984(15)	0.01548(6)	0.0300(4)

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.94 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The highest peak (0.84 e Å^{-3}) and the

***Corresponding author: Kwang Ha,** Chonnam National University, School of Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea, e-mail: hakwang@chonnam.ac.kr

deepest hole (-0.50 e Å^{-3}) in the difference Fourier map are located 0.83 Å and 0.67 Å from the atom S1, respectively.

Discussion

This contribution is part of my continuing interest in the structural chemistry of 2,2′-bipyrimidine metal complexes [1–8]. The title complex *cis*-[Ni(NCS)$_2$(bpym)$_2$] is disposed about a twofold rotation axis running in the [001] direction passing through the Ni atom: the asymmetric unit contains one half of the complex. In the complex, the central Ni(II) is six-coordinated by four pyrimidine N atoms from two chelating bpym ligands and two mutually *cis*-positioned N atoms from two SCN^- anionic ligands in a distorted octahedral manner. The main contribution to the distortion of the octahedron is made by the tight chelate angle $<$ N1—Ni1—N4 = 78.23(6)°, which results in non-linear trans axes ($<$ N1—Ni1—N1^i = 176.06(8)° and $<$ N4—Ni1—N5^i = 172.19(6)°; symmetry code i: $1-x$, $1/2-y$, z). The Ni—N bond lengths are almost equal (2.062(2)–2.095(2) Å), but the Ni—N bond *trans* to the NCS ligand (2.095(2) Å) is slightly longer than the Ni—N bond trans to the bpym ligand (2.071(1) Å), because of the different trans effects of the ligands. The thiocyanato ligand is almost linear displaying N—C—S bond angle of 178.5(2)°, and the N atom is bent coordinated to the Ni atom with the Ni—N—C(NCS) bond angle of 164.0(2)°, characteristic of an N-bonded conformation. The bpym ligand is nearly planar and the dihedral angle between the least-squares planes of the two bpym ligands is 71.96(3)°. The two pyrimidine rings of the bpym ligand are nearly parallel with the dihedral angle of 4.7(1)° between the ring planes. In the crystal structure, several intermolecular π-π interactions between adjacent pyrimidine rings of the lignad are present. The shortest distance between Cg1 (the centroid of ring N1—C4) and Cg1^{ii} (ring N3—C6; symmetry code ii: $5/4-y$, $1/4+x$, $1/4-z$) is 4.672(1) Å, and the dihedral angle between the ring planes is 48.89(9)°.

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