Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

N,*N*′-Bis[2-(methylsulfanyl)phenyl]pyridine-2,6-dicarboxamide

Sheng-Gui Liu, Yi-Zhi Li,* Jing-Lin Zuo* and Xiao-Zeng You

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: llyyjz@nju.edu.cn

Received 30 June 2004
Accepted 27 July 2004
Online 13 August 2004

In the title compound, $C_{21}H_{19}N_3O_2S_2$, there are intramolecular hydrogen bonds and steric strain. Hydrogen bonds involving the amide groups and the pyridine N atoms force the two carboxamide groups and the central pyridine ring into the same plane (r.m.s. deviation = 0.054 Å). Steric strain between the two methylsulfanyl substituents results in the benzene rings of the two arms of the ligand being inclined to one another by 45.23 (9)°. In the crystal structure, intermolecular C—H···O interactions are present and lead to the formation of a three-dimensional network.

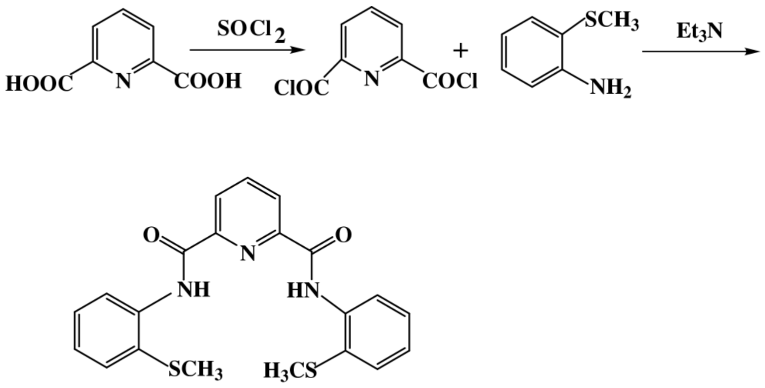
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.047
wR factor = 0.103
Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In recent years, investigation of the coordination chemistry of high oxidation state metal ions with non-macrocyclic chelating ligands has attracted much attention from bioinorganic chemists in order to provide models for the Ni sites in (NiFe)-hydrogenases (Collins *et al.*, 1991). Deprotonated amide N atoms with good σ-donor properties are capable of stabilizing the high oxidation state of metal ions to a considerable extent (Kawamoto *et al.*, 1998; Marlin *et al.*, 1999; Patra *et al.*, 2000). In order to develop further the coordination chemistry of amide ligands towards metal ions, new ligands must be exploited. We describe here the synthesis and crystal structure analysis of *N*,*N*′-bis[2-(methylsulfanyl)phenyl]pyridine-2,6-dicarboxamide, (I).



(I)

The molecular structure of (I) is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The bond lengths and angles are all within normal ranges. The N—C bond distances for N1—C7 [1.342 (3) Å] and N3—C13 [1.350 (3) Å] are similar to that in 2,6-bis[(6-methyl-2-pyridinyl)carbamoyl]pyridine [1.352 (4) Å; Redmore *et al.*, 1997]. The amide and pyridine N atoms and the two S atoms appended to the benzene rings are all directed towards the

DOI: 10.1107/S1600536804018409

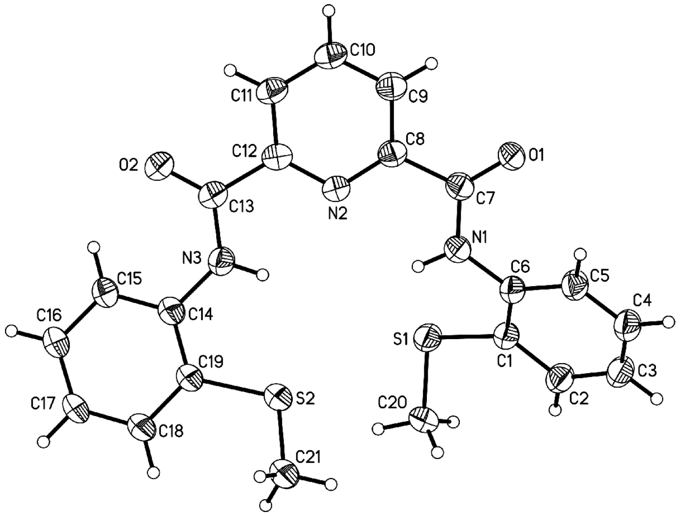


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level.

center of the molecular cavity. The carbonyl groups are directed outside the cavity. The intramolecular hydrogen bonds N1—H1···N2 [2.726 (3) Å] and N3—H3···N2 [2.712 (3) Å] force the two carboxamide groups and the central pyridine ring to be in the same plane (r.m.s. deviation = 0.054 Å). Details of the hydrogen bonding are given in Table 2. Steric strain between the two methylsulfanyl substituents causes the two benzene rings in the two arms of the ligand to be inclined to one another by an angle of 45.23 (9)°.

The crystal packing of the title compound is shown in Fig. 2. Weak C—H···O interactions [C2—H2···O1^{i} = 3.374 (3) Å; see Table 2 for details and symmetry codes] link the molecules into a one-dimensional chain. The chains are linked by another weak C—H···O interaction [C20—H20*C*···O2^{ii} = 3.447 (3) Å], which results in the formation of a three-dimensional structure.

Experimental

The title compound was prepared by refluxing pyridine-2,6-dicarboxylic acid (3.34 g, 20 mmol) in thionyl chloride (10 ml) for 8 h. Excess thionyl chloride was removed under vacuum. After cooling to room temperature, 2-(methylsulfanyl)aniline (5.56 g, 40 mmol) and triethylamine (3 ml) in CH_2Cl_2 (40 ml) were added to the residue. The mixture was stirred for 2 h, then the solvent was removed under reduced pressure. On recrystallization from ethanol, colourless crystals were obtained (yield: 7.40 g, 90.5%). Analysis calculated for $C_{21}H_{19}N_3O_2S_2$: C 61.54, H 4.64, N 10.26%; found: C 61.62, H 4.63, N 10.29%. IR (cm^{-1}): 3450, 3170, 1676, 1655, 1585, 1533, 1458, 1257, 1073, 768.

Crystal data

$C_{21}H_{19}N_3O_2S_2$
M_r = 409.51
Monoclinic, $P2_1/n$
a = 8.8370 (18) Å
b = 15.488 (3) Å
c = 15.155 (3) Å
β = 105.87 (3)°
V = 1995.2 (7) Å^3
Z = 4
D_x = 1.363 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3499 reflections
θ = 1.3–2.6°
μ = 0.29 mm^{-1}
T = 293 (2) K
Prism, colourless
0.35 × 0.22 × 0.21 mm

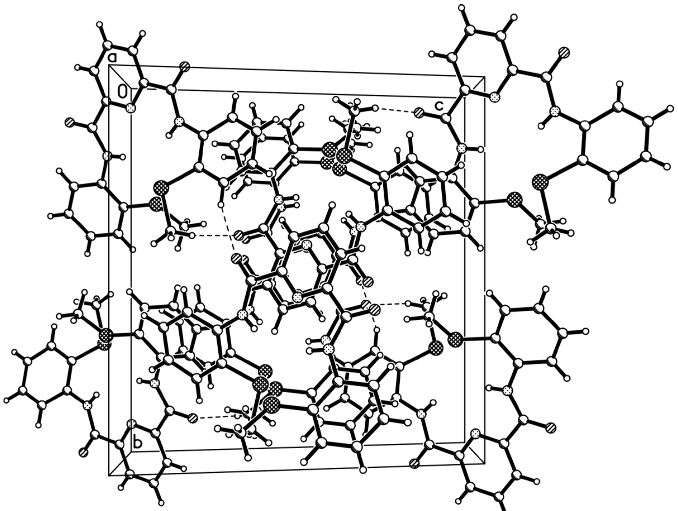


Figure 2
The crystal packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*XPREP*; Bruker, 2000)
T_{min} = 0.93, T_{max} = 0.94
3742 measured reflections
3499 independent reflections
2135 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 25.0°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.103
S = 1.07
3499 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.771 (3)	S2—C19	1.793 (3)
S1—C20	1.780 (3)	N1—C7	1.342 (3)
S2—C21	1.643 (3)	N3—C13	1.350 (3)
C1—S1—C20	104.59 (13)	C21—S2—C19	106.47 (14)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S1	0.86	2.59	2.924 (2)	104
N1—H1···N2	0.86	2.31	2.726 (3)	110
N3—H3···S2	0.86	2.45	2.924 (2)	115
N3—H3···N2	0.86	2.28	2.712 (3)	111
C2—H2···O1^{i}	0.93	2.50	3.374 (3)	156
C20—H20*C*···O2^{ii}	0.96	2.52	3.448 (3)	163

Symmetry codes: (i) $\frac{5}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

The H atoms were included in calculated positions and treated as riding atoms; bond distances were 0.93 Å for aromatic H atoms and 0.86 Å for amine H atoms, with $U_{iso}(H) = 1.2U_{eq}(C,N)$; 0.96 Å for methyl H atoms, with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *XSCANS* (Bruker, 2000); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by The Major State Basic Research Development Program (G2000077500) and the National Natural Science Foundation of China (NSF20201006 and 90101028).

References

Bruker (2000). *XPREP, XSCANS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Collins, T. J., Nichols, T. N. & Uffelman, E. S. (1991). *J. Am. Chem. Soc.* **113**, 4708–4709.

Kawamoto, T., Hamme, B. S., Ostrander, R., Rheingold, A. L. & Borovik, A. S. (1998). *Inorg. Chem.* **37**, 3424–3427.

Marlin, D., Olmstead, M. M. & Mascharak, P. K. (1999). *Inorg. Chem*, **38**, 3258–3260.

Patra, A. K., Ray, M. & Mukherjee, R. (2000). *Polyhedron*, **19**, 1423–1428.

Redmore, S. M., Rickard, C. E. F., Webb, S. J. & Wright, L. J. (1997). *Inorg. Chem.* **36**, 4743–4748.