Yang Liguo*, Shi Juntao, Zhang Zhen, Wang Fang and Tian Dayong

The crystal structure of (2Z,2'Z)-N',N''''-(pyridine-2,6-dicarbonyl)dipicolinohydrazonamide, C₁₉H₁₇N₉O₂

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Abstract

C₁₉H₁₇N₉O₂, monoclinic, *C*2/*c* (no. 15), *a* = 20.297(7) Å, *b* = 10.122(3) Å, *c* = 9.078(3) Å, β = 95.675(4)°, *V* = 1856.0(10) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0467, *wR*_{ref}(*F*²) = 0.1205, *T* = 296(2) K [1–3].

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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.

*Corresponding author: Yang Liguo, College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P.R. China, e-mail: lgyang@ayit.edu.cn. <https://orcid.org/0000-0003-4899-8298>

Shi Juntao, Zhang Zhen, Wang Fang and Tian Dayong: College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P.R. China

Table 1: Data collection and handling.

Crystal:	White block
Size:	0.08 × 0.06 × 0.04 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.10 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	27.7°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	16459, 2160, 0.045
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 1544
<i>N</i> (<i>param</i>) _{refined} :	137
Programs:	Bruker programs [1], SHELX [2, 3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	0.39649(7)	0.77301(12)	0.53863(13)	0.0503(4)
N1	0.35830(7)	0.16154(13)	0.50580(16)	0.0437(4)
N2	0.39799(7)	0.50154(13)	0.51742(15)	0.0386(4)
N3	0.43094(7)	0.58705(13)	0.42960(15)	0.0397(4)
H3	0.4533	0.5552	0.3622	0.048*
N4	0.5000	0.72678(17)	0.2500	0.0327(4)
N5	0.40495(9)	0.34440(15)	0.32842(16)	0.0548(5)
H5A	0.4254	0.3970	0.2741	0.066*
H5B	0.3958	0.2652	0.2987	0.066*
C1	0.5000	1.0012(2)	0.2500	0.0397(5)
H1	0.5000	1.0931	0.2500	0.048*
C2	0.46444(8)	0.93226(16)	0.34627(17)	0.0366(4)
H2	0.4396	0.9766	0.4116	0.044*
C3	0.46643(8)	0.79537(15)	0.34374(16)	0.0328(4)
C4	0.42836(8)	0.71826(15)	0.44852(16)	0.0353(4)
C5	0.38730(8)	0.38596(16)	0.46000(17)	0.0348(4)
C6	0.35362(8)	0.28738(15)	0.54807(17)	0.0345(4)
C7	0.31835(8)	0.32597(18)	0.66369(19)	0.0420(4)
H7	0.3158	0.4146	0.6896	0.050*
C10	0.32888(10)	0.07085(18)	0.5834(2)	0.0524(5)
H10	0.3327	−0.0175	0.5573	0.063*
C9	0.29333(10)	0.1010(2)	0.6996(2)	0.0570(5)
H9	0.2737	0.0344	0.7508	0.068*
C8	0.28721(9)	0.2308(2)	0.7394(2)	0.0539(5)
H8	0.2624	0.2539	0.8163	0.065*

Source of material

2,6-Pyridinedicarboxylic acid dihydrazide (0.010 mol) was added to a methanolic solution (30 mL) of the methyl ester of

iminopyrazine-2-carboxylic acid (2.6 g, 0.025 mol), prepared *in situ* from 2-cyanopyrazine and sodium metal (stirred at room temperature for 12 h). The mixture was refluxed for 24 h with the formation of a yellow powder. The solid was filtered off, washed with water, methanol and ether and dried under vacuum. Yield (6.5 g, 80%) m.p. 253–259 K. FTIR (KBr) ν (cm⁻¹): 3200, 1693, 1564, 1466, 1257, 1041. Anal. Calc. for C₁₉H₁₇N₉O₂(%): C, 56.58; H, 4.22; N, 31.27. Found (%): C, 56.61; H, 4.25; N, 31.30.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5 U_{\text{eq}}(\text{C})$. The N-bound H atoms were located in a difference Fourier map but were refined riding on the parent atom with $U_{\text{iso}}(\text{H})$ set to 1.2 $U_{\text{equiv}}(\text{N})$ [1–3].

Discussion

Tritopic ligands with a 2,6-pyridine dihydrazone are interesting ligands as there are seven potentially coordinated atoms. So polynuclear metal complexes can be synthesized with 2,6-pyridine dihydrazone. Lots of complexes containing tritopic ligands have been reported which have been identified by X-ray crystallography, and include mononuclear, dinuclear, hexanuclear, heptanuclear, and mononuclear examples. Some of these could be components in grid assembly or further examples in a potentially vast library of different complexes which could form as a result of the dynamic nature of the metal-ligand interaction, the flexibility of the ligands, and their different possible bonding conformations. The complex containing the ligands 2noap have been reported, but the structure of the ligand 2noap has not been reported [4–7].

As shown in the figure, the title compound crystallizes in the monoclinic space group *C2/c* with four formula units in the unit cell. Thus, the title molecule is located on a twofold axis. The bond lengths of N2=C5, N2–C3 and C3–N4 are 1.290, 1.396 and 1.337 Å, respectively, which are similar to a literature known structure. The atoms N1, N2, O1, N4, are the coordinating atoms of the ligand, one ligand will coordinate with three metal atoms. The transition metal complexes have been reported, but the rare earth metal complexes have not been reported, our group will do this job in the future. This sentence was added after [8–16].

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