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The crystal structure of poly $[(\mu_3\text{-}N^1, N^4\text{-bis(pyridin-3-yl)cyclohexane-1,4-dicarboxamide-}\kappa^3\text{-O:N:N'})\text{-}(p\text{-toluenesulfonato-}\kappa^2\text{O,O'})\text{silver(I)}]$, $\text{C}_{25}\text{H}_{27}\text{Ag}_1\text{N}_4\text{O}_5\text{S}$

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Abstract

$(\text{C}_{25}\text{H}_{27}\text{AgN}_4\text{O}_5\text{S})_n$, monoclinic, $P2_1/c$ (no. 14), $a = 8.4459(2)$ Å, $b = 23.8845(5)$ Å, $c = 13.0653(3)$ Å, $\beta = 105.096(2)^\circ$, $V = 2544.66(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0315$, $wR_{\text{ref}}(F^2) = 0.0689$, $T = 293(2)$ K.

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A part of the title structure is shown in the figure (The asymmetric unit is labelled). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.20 × 0.12 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.92 mm ^{−1}
Diffractometer, scan mode:	Gemini S Ultra, φ and ω
θ_{max} , completeness:	30.2°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13415, 6285, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3711
$N(\text{param})_{\text{refined}}$:	326
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

Source of material

The educt 1,4-cyclohexanedicarboxylic (1.72 g, 10 mmol) acid was added into a flask, 10 mL SOCl₂ was also added under

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}
Ag1	0.87622(2)	0.07388(2)	0.54722(2)	0.03738(7)
O1	1.4280(3)	−0.09596(8)	0.96063(15)	0.0764(8)
O2	0.2509(2)	−0.12719(8)	0.32635(12)	0.0424(5)
N1	1.0687(2)	0.04319(9)	0.68676(14)	0.0324(5)
N2	1.2359(3)	−0.08921(8)	0.80436(14)	0.0345(5)
H2	1.173841	−0.108877	0.754677	0.041*
N3	0.6552(2)	0.03952(8)	0.43289(14)	0.0318(5)
N4	0.5208(2)	−0.10460(8)	0.38043(13)	0.0320(5)
H4	0.617676	−0.118653	0.400474	0.038*
C1	1.0927(3)	−0.01102(10)	0.71065(17)	0.0313(6)
H1	1.020065	−0.036838	0.670421	0.038*
C2	1.2207(3)	−0.03099(10)	0.79255(16)	0.0325(6)
C3	1.3252(3)	0.00811(11)	0.85511(17)	0.0400(7)
H3	1.411460	−0.003337	0.911249	0.048*
C4	1.2977(3)	0.06414(11)	0.83176(18)	0.0413(7)
H4A	1.364405	0.091065	0.873187	0.050*
C5	1.1722(3)	0.08003(11)	0.74756(17)	0.0363(6)
H5	1.157854	0.117953	0.731681	0.044*
C6	1.3373(3)	−0.11857(12)	0.88509(19)	0.0410(7)
C7	1.3252(3)	−0.18119(11)	0.87059(17)	0.0349(6)
H7	1.211876	−0.190103	0.832694	0.042*
C8	1.4360(3)	−0.20218(11)	0.80370(18)	0.0380(6)
H8A	1.408526	−0.182934	0.735985	0.046*
H8B	1.549179	−0.193530	0.839305	0.046*
C9	1.4183(3)	−0.26471(11)	0.78511(18)	0.0378(6)
H9A	1.498325	−0.277007	0.748466	0.045*
H9B	1.310080	−0.272489	0.739545	0.045*
C10	0.5260(3)	0.06810(10)	0.37306(17)	0.0359(6)
H10	0.529231	0.107024	0.373848	0.043*
C11	0.3900(3)	0.04182(12)	0.31115(18)	0.0411(7)
H11	0.303672	0.062950	0.270705	0.049*
C12	0.3810(3)	−0.01590(12)	0.30874(17)	0.0382(6)
H12	0.289955	−0.034064	0.266337	0.046*
C13	0.5111(3)	−0.04623(10)	0.37108(17)	0.0301(6)
C14	0.6441(3)	−0.01647(11)	0.43060(16)	0.0305(6)
H14	0.731797	−0.036717	0.471841	0.037*
C15	0.3945(3)	−0.14136(11)	0.36144(17)	0.0371(6)
C16	0.4421(3)	−0.20176(10)	0.38794(17)	0.0337(6)
H16	0.558127	−0.203177	0.426806	0.040*
C17	0.3399(4)	−0.22566(11)	0.45816(18)	0.0442(7)
H17A	0.369254	−0.206653	0.526103	0.053*
H17B	0.224921	−0.218298	0.425474	0.053*
C18	0.3641(4)	−0.28791(11)	0.47616(18)	0.0466(7)
H18A	0.292932	−0.301342	0.518361	0.056*
H18B	0.476675	−0.295328	0.514931	0.056*
S1	1.06936(8)	0.16516(3)	0.43285(4)	0.03396(16)
O3	1.1451(2)	0.13711(7)	0.53140(12)	0.0484(5)
O4	0.8998(2)	0.14784(8)	0.39688(16)	0.0673(6)
O5	1.1591(3)	0.15857(8)	0.35532(15)	0.0788(8)
C19	1.0681(3)	0.23675(10)	0.46282(15)	0.0281(6)
C20	1.0213(3)	0.27581(11)	0.38118(17)	0.0327(6)
H20	0.996559	0.263967	0.310985	0.039*
C21	1.0116(3)	0.33153(11)	0.4038(2)	0.0403(7)
H21	0.977388	0.356824	0.348289	0.048*
C22	1.0515(3)	0.35126(11)	0.5075(2)	0.0412(7)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C23	1.0973(3)	0.31225(12)	0.58842(19)	0.0399(7)
H23	1.123423	0.324304	0.658516	0.048*
C24	1.1048(3)	0.25597(11)	0.56699(17)	0.0352(6)
H24	1.134572	0.230561	0.622639	0.042*
C25	1.0453(4)	0.41284(12)	0.5306(3)	0.0679(10)
H25A	1.141714	0.430780	0.520273	0.102*
H25B	1.040588	0.417981	0.602575	0.102*
H25C	0.949664	0.429053	0.483504	0.102*

stirring. After 10 min, the reaction mixture was heated at reflux for 3 h. At the end of reaction, the excess SOCl₂ was removed by distillation. A white solid was obtained. After that 20 mL anhydrous THF was added into the flask, then the mixture was allowed to cool to room temperature and then cooled with an ice bath for 30 min. A mixture of 3-aminopyridine (2.07 g, 22 mmol), 5 mL triethylamine and 20 mL anhydrous THF was added drop by drop into the flask under strongly stirring. There is a lot of white precipitate appear during dropping. After finishing dropping, the ice bath was removed. Then the reaction mixture was allowed to warm up to room temperature and stayed for 12 h. After the reaction was complete, the crude product was filtered, and washed with THF (20 mL*2), water (20 mL*2), a white solid was obtained after dried in vacuum, and then was recrystallized in a mixed solvent of methanol and water. Yield, 0.88 g (54%, based on 1, 4-cyclohexanedicarboxylic). The title compound was dissolved into mixed solvents of methanol and water, and then stayed at room temperature. Colorless block crystal were obtained after two weeks. Elemental Analysis calcd. (%) for C₁₈H₂₀N₄O₂: C, 66.65; H, 6.21; N, 17.27; Found: C, 66.25; H, 6.62; N, 16.93. ¹H-NMR (300 MHz, DMSO-*d*₆): δ (ppm) 10.07 (s, 2.00H), 8.73 (s, 2.00H), 8.21 (s, 2.00H), 8.02 (d, *J* = 7.8 Hz, 2.00H), 7.36–7.24 (m, 2.00H), 2.38 (brs, 2.00H), 2.01–1.86 (m, 4.00H), 1.59–1.39 (m, 4.00H); IR (cm^{−1}): 3226(w), 3167(w), 3032(w), 2967(m), 2947(m), 2935(m), 2902(w), 2864(w), 1683(vs), 1598(w), 1581(s), 1536(s), 1476(m), 1453(m), 1423(vs), 1375(w), 1338(w), 1264(s), 1244(w), 1193(w), 1160(m), 802(m), 707(m), 630(w), 595(vw). ESI-MS (*m/z*): [M + H]⁺ calcd. for C₁₈H₂₀N₄O₂, 324.38; found, 325.20. Reaction of this organic compound with a silver(I) salt in the presence *p*-toluenesulfonic acid gave same crystals of the title compound.

Experimental details

X-ray diffraction data for the title structure were collected on Oxford Diffraction Xcalibur by CrysAlis^{PRO} [1]. The structure was solved with the ShelXT [2] structure solution program and refined with the XL [3] refinement package. The positions of

the hydrogen atoms were generated geometrically. The figure was drawn by Diamond [4].

Comment

Pyridyl-based ligand plays an important role for construction of coordination polymer [5]. Among them, semi-rigid bis-pyridyl-amide ligands are known for their rich coordination modes to attract much attention from crystal engineering scientist [6]. However, only limited number of coordination polymers based on N^1,N^4 -bis(pyridin-3-yl)cyclohexane-1,4-dicarboxamide [7–13] are reported. To the best of our knowledge, the single crystal structure of N^1,N^4 -bis(pyridin-3-yl)cyclohexane-1,4-dicarboxamide-based silver coordination polymer has not been reported so far.

The title compound crystallized in space group $P2_1/c$ and an asymmetric unit contains one Ag^+ ion, one N^1,N^4 -bis(pyridin-3-yl)cyclohexane-1,4-dicarboxamide and one *p*-toluenesulfonate. The bond lengths and angles within these moieties are in the expected ranges. Ag^+ is coordinated by two N and one O atom from three dicarboxamide ligands (see the figure). The distance of Ag1-N1, Ag1-N3 and Ag1-O2 is 2.227(2) Å, 2.222(2) Å and 2.535(2) Å, respectively. It is worth noting that O2 and O4 from *p*-toluenesulfonate also coordinate the Ag^+ ion with distance of Ag1-O2, Ag1-O4 is 2.687(2) Å and 2.779(2) Å, respectively. In the perspective of topology analysis, each three-coordinated Ag^+ ion serves as a three-connected node and N^1,N^4 -bis(pyridin-3-yl)cyclohexane-1,4-dicarboxamide acting as a trinodal building block result in a two-dimensional layer, which can be described as a uninodal three-connected **fes** net with the point symbol of $(4,8^2)$ [14].

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