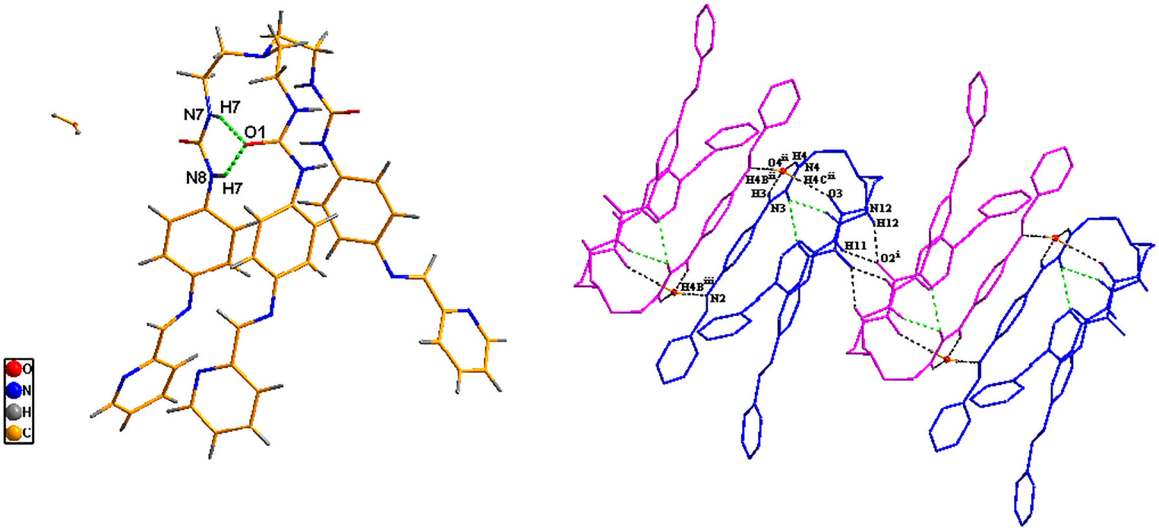
Jie Li*, Yinghan Dong, Mengying Qiu, Haiwei Han and Xiaoyan Pei

Crystal structure of 1,1′,1″-(nitrilotris(ethane-2,1-diyl))tris(3-(4-(((*E*)-pyridin-2-ylmethylene) amino)phenyl)urea), $C_{45}H_{47}N_{13}O_4$



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Abstract

$C_{45}H_{47}N_{13}O_4$, triclinic, $P\bar{1}$ (no. 2), a = 10.242(6) Å, b = 14.766(15) Å, c = 15.503(8) Å, α = 70.91(2)°, β = 88.052(16)°, γ = 74.13(3)°, V = 2127(3) Å^3, Z = 2, $R_{gt}(F)$ = 0.0411, $wR_{ref}(F^2)$ = 0.1059, T = 120(2) K.

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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:	0.33 × 0.29 × 0.21 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	52751, 7782, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 6364
$N(param)_{refined}$:	567
Programs:	Bruker,[1] SHELX,[2–4] Diamond[5]

1 Source of material

The target compound was synthesized in three synthetic steps. Fistly, a solution of tris(2-aminoethyl) amine (0.7 g, 4.79 mmol) in 15 mL of THF was added dropwise to a solution of *p*-nitroisocyanate(2.15 g, 13.10 mmol) in THF (15 mL). After refluxing under intensive stirring for 4 h, the precipitate was filtered off and washed several times with THF and diethyl ether and then dried in vacuum to yield analytically pure 1,1′,1″-(nitrilotris (ethane-2,1-diyl))tris(3-(4-nitrophenyl)urea) (La) as a yellow solid. Secondly, hydrazine monohydrate (11 mL) was added dropwise to the suspension of La and Pd/C 10 % (0.2 g, cat.) in ethanol (70 mL). After refluxing under stirring for 12 h, the solid was filtered off via suction filtration and dissolved in DMF (10 mL) and filtered through Celite to remove Pd/C. The DMF solution was poured in water (150 mL), and the precipitate thus obtained was filtered off,

***Corresponding author: Jie Li**, College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang, Henan 464000, P.R. China, E-mail: lijie@xynu.edu.cn. https://orcid.org/0000-0002-3104-1222
Yinghan Dong, Mengying Qiu, Haiwei Han and Xiaoyan Pei, College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang, Henan 464000, P.R. China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1229 (2)	0.57380 (16)	0.89109 (14)	0.0480 (5)
H1	0.1185	0.5069	0.9170	0.058*
C2	0.0670 (2)	0.63972 (16)	0.93716 (14)	0.0463 (5)
H2	0.0255	0.6187	0.9932	0.056*
C3	0.0731 (2)	0.73690 (15)	0.89974 (13)	0.0409 (5)
H3A	0.0351	0.7843	0.9294	0.049*
C4	0.13507 (18)	0.76437 (14)	0.81866 (13)	0.0344 (4)
H4A	0.1407	0.8309	0.7918	0.041*
C5	0.18915 (17)	0.69335 (13)	0.77670 (12)	0.0286 (4)
C6	0.26186 (16)	0.71486 (12)	0.69186 (11)	0.0271 (4)
H6	0.2786	0.6692	0.6588	0.032*
C7	0.37492 (16)	0.81085 (11)	0.58017 (11)	0.0241 (3)
C8	0.47468 (16)	0.86042 (12)	0.57503 (11)	0.0259 (4)
H8A	0.4911	0.8811	0.6246	0.031*
C9	0.54994 (16)	0.87982 (11)	0.49854 (11)	0.0253 (4)
H9	0.6200	0.9111	0.4973	0.030*
C10	0.52385 (16)	0.85388 (11)	0.42338 (11)	0.0242 (3)
C11	0.42126 (16)	0.80661 (12)	0.42711 (11)	0.0257 (4)
H11A	0.4010	0.7898	0.3760	0.031*
C12	0.34909 (16)	0.78423 (12)	0.50502 (11)	0.0256 (4)
H12A	0.2815	0.7505	0.5074	0.031*
C13	0.63265 (15)	0.83286 (11)	0.28296 (11)	0.0231 (3)
C14	0.74692 (16)	0.83580 (12)	0.13970 (11)	0.0254 (4)
H14A	0.7114	0.8892	0.0809	0.030*
H14B	0.7054	0.7811	0.1454	0.030*
C15	0.89992 (16)	0.79658 (12)	0.13731 (10)	0.0244 (3)
H15A	0.9203	0.7812	0.0799	0.029*
H15B	0.9423	0.8496	0.1365	0.029*
C16	0.3423 (2)	0.24864 (14)	1.05648 (12)	0.0372 (4)
H16	0.2784	0.2106	1.0693	0.045*
C17	0.4215 (2)	0.24448 (16)	1.12856 (13)	0.0415 (5)
H17	0.4151	0.2024	1.1889	0.050*
C18	0.5101 (2)	0.30298 (18)	1.11089 (13)	0.0471 (5)
H18	0.5629	0.3043	1.1595	0.057*
C19	0.52137 (19)	0.35978 (15)	1.02157 (13)	0.0380 (4)
H19	0.5819	0.4005	1.0077	0.046*
C20	0.44196 (17)	0.35580 (13)	0.95284 (12)	0.0290 (4)
C21	0.45851 (17)	0.40499 (13)	0.85516 (12)	0.0303 (4)
H21	0.4000	0.4029	0.8100	0.036*
C22	0.57436 (16)	0.48457 (12)	0.73628 (11)	0.0273 (4)
C23	0.61822 (18)	0.57036 (13)	0.70348 (12)	0.0310 (4)
H23	0.6231	0.6071	0.7428	0.037*
C24	0.65458 (17)	0.60251 (12)	0.61459 (12)	0.0295 (4)
H24	0.6805	0.6627	0.5924	0.035*
C25	0.65363 (16)	0.54762 (12)	0.55702 (11)	0.0253 (4)
C26	0.61028 (16)	0.46152 (12)	0.58894 (11)	0.0262 (4)
H26	0.6089	0.4237	0.5500	0.031*
C27	0.56915 (16)	0.43083 (12)	0.67754 (11)	0.0271 (4)
H27	0.5373	0.3731	0.6984	0.033*
C28	0.79690 (17)	0.52882 (12)	0.42935 (11)	0.0275 (4)
C29	0.93707 (17)	0.53848 (12)	0.29665 (11)	0.0272 (4)
H29A	0.9317	0.4763	0.2876	0.033*
H29B	1.0214	0.5233	0.3343	0.033*
C30	0.93950 (17)	0.61702 (12)	0.20476 (11)	0.0251 (4)
H30A	1.0130	0.5889	0.1699	0.030*
H30B	0.8521	0.6349	0.1694	0.030*
C31	0.8287 (2)	1.07287 (14)	0.97354 (13)	0.0376 (4)
H31	0.8962	1.0826	1.0074	0.045*
C32	0.6957 (2)	1.10197 (14)	0.99386 (14)	0.0391 (4)
H32	0.6717	1.1328	1.0394	0.047*
C33	0.5976 (2)	1.08547 (15)	0.94679 (15)	0.0448 (5)
H33	0.5046	1.1047	0.9595	0.054*
C34	0.63602 (19)	1.04073 (14)	0.88102 (13)	0.0380 (4)
H34	0.5705	1.0273	0.8486	0.046*
C35	0.77240 (18)	1.01576 (12)	0.86316 (12)	0.0295 (4)
C36	0.82269 (19)	0.97185 (13)	0.79089 (12)	0.0329 (4)
H36	0.9039	0.9821	0.7631	0.039*
C37	0.81548 (17)	0.88400 (13)	0.69330 (12)	0.0297 (4)
C38	0.85181 (19)	0.94384 (13)	0.61197 (12)	0.0331 (4)
H38	0.8391	1.0126	0.6028	0.040*
C39	0.90614 (19)	0.90572 (13)	0.54384 (12)	0.0327 (4)
H39	0.9285	0.9484	0.4883	0.039*
C40	0.92789 (16)	0.80457 (12)	0.55697 (12)	0.0269 (4)
C41	0.88951 (17)	0.74470 (12)	0.63807 (12)	0.0301 (4)
H41	0.9025	0.6759	0.6475	0.036*
C42	0.83304 (17)	0.78349 (13)	0.70487 (12)	0.0314 (4)
H42	0.8060	0.7416	0.7590	0.038*
C43	1.02303 (17)	0.80029 (12)	0.40722 (11)	0.0267 (4)
C44	1.13525 (18)	0.76380 (12)	0.27554 (11)	0.0288 (4)
H44A	1.2328	0.7615	0.2728	0.035*
H44B	1.0815	0.8332	0.2431	0.035*
C45	1.10698 (16)	0.69522 (12)	0.22837 (11)	0.0250 (4)
H45A	1.1476	0.7087	0.1682	0.030*
H45B	1.1516	0.6252	0.2655	0.030*
N1	0.18307 (16)	0.59884 (11)	0.81175 (11)	0.0375 (4)
N2	0.30294 (13)	0.79322 (10)	0.66151 (9)	0.0256 (3)
N3	0.59786 (14)	0.88215 (10)	0.34524 (9)	0.0275 (3)
H3	0.6241	0.9364	0.3356	0.033*
N4	0.70468 (14)	0.87530 (10)	0.21420 (9)	0.0256 (3)
H4	0.7268	0.9287	0.2145	0.031*
N5	0.35014 (15)	0.30280 (11)	0.96983 (10)	0.0336 (3)
N6	0.54983 (15)	0.45011 (11)	0.83051 (10)	0.0305 (3)
N7	0.69215 (14)	0.58263 (10)	0.46540 (9)	0.0300 (3)
H7	0.6460	0.6423	0.4299	0.036*
N8	0.81914 (14)	0.57647 (10)	0.34294 (9)	0.0296 (3)
H8	0.7599	0.6333	0.3128	0.036*
N9	0.86900 (15)	1.03132 (12)	0.90843 (11)	0.0365 (4)
N10	0.76015 (15)	0.92080 (11)	0.76502 (10)	0.0325 (3)
N11	0.98874 (15)	0.75750 (10)	0.49445 (10)	0.0302 (3)
H11	1.0073	0.6920	0.5138	0.036*
N12	1.10057 (15)	0.73460 (10)	0.37031 (9)	0.0302 (3)
H12	1.1313	0.6717	0.4049	0.036*
N13	0.96127 (13)	0.70735 (9)	0.21468 (9)	0.0216 (3)
O1	0.60037 (11)	0.75569 (8)	0.28979 (7)	0.0256 (3)
O2	0.86489 (14)	0.44333 (9)	0.47375 (8)	0.0397 (3)
O3	0.98820 (13)	0.89132 (8)	0.36622 (8)	0.0342 (3)
O4	0.75066 (14)	0.02647 (10)	0.28975 (9)	0.0341 (3)
H4B	0.735 (2)	0.0799 (18)	0.3028 (15)	0.057 (7)*
H4C	0.831 (3)	−0.016 (2)	0.3181 (17)	0.074 (8)*

washed several times with ethanol and diethyl ether and dried to give analytically pure 1,1′,1″-(nitrilotris(ethane-2,1-diyl))tris(3-(4-aminophenyl)urea) (Lb) as a white solid. Lastly, 2-pyridylaldehyde was added to a solution of Lb in 5 mL of DMSO stirring at room temperature for 12 h. Subsequently, the precipitate was filtered, and washed several times with acetonitrile and diethyl ether, and dried over vacuum to get the target compound (L) as a yellow solid (0.48 g, 0.59 mmol, 80 %). At room temperature, yellow block crystals of L were obtained by ether diffusion method.

2 Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.96 Å (methyl), U_{iso} (H) = 1.5 U_{eq}(C), C–H = 0.98 Å (methine), U_{iso}(H) = 1.2 U_{eq}(C), C–H = 0.93 Å (aromatic and alkenyl), U_{iso}(H) = 1.2 U_{eq}(C), and O–H = 0.82 Å (hydroxyl), U_{iso}(H) = 1.5 U_{eq}(O).

3 Comment

Over the past few decades, tripodal urea derivatives have been proved to be a class of excellent anion receptors since the tripodal framework offers a greater opportunity for the spatially adaptive encapsulation of anions with size- and shape-complementarity than linear receptors.[6–14] Such receptors typically contain three or six urea units, which can effectively bind with anions through multiple hydrogen bonds, making them valuable in various applications including anion extraction,[8,9] anion recognition[10–12] and transmembrane transport.[13] In this study, a novel imine-pyridine-functionalized tripodal tris(urea) receptor was prepared and its structure confirmed by single crystal X-ray diffraction.

The asymmetric structural unit contains one title molecule (see left part of the figure) and one lattice water molecule. In the tripodal structure, NH groups on two urea units point towards the outside of the cavity, while NH groups on the other urea unit point towards the inside of the cavity. The two urea groups pointing in the same direction form two intramolecular hydrogen bonds of N7–H7···O1($d_{N7\cdots O1}$ = 3.020 Å, 148.49°), and N8–H8···O1($d_{N8\cdots O2}$ = 2.854 Å, 159.04°). Moreover, there are six intermolecular hydrogen bonds formed by three urea units and the water molecule. Among them, O4 atom from lattice water takes part in four intermolecular hydrogen bonds with three urea units, viz. $N3^{ii}$ – $H3^{ii}$···O4, $N4^{ii}$ – $H4^{ii}$···O4, O4–H4C···$O3^{ii}$ and O4–H4B···$N2^{iii}$ (symmetry code: (ii) x, $y + 1$, z; (iii) $-x + 2$, $-y + 1$, $-z + 1$). Meanwhile, O2 atom from one urea unit takes part in two intermolecular hydrogen bonds with another urea unit from the adjacent molecule, viz. $N11^{i}$ – $H11^{i}$···O2 and $N12^{i}$ – $H12^{i}$···O2 (symmetry code: (i) $-x + 2$, $-y + 1$, $-z + 1$). The distance of N7···O1 is in the range of 2.702–2.984 Å and the angle of the intermolecular hydrogen bonds is in the range of 148.91–177.43°. The intermolecular hydrogen bonds contribute to the formation of a one-dimensional chain in the crystal structure (right part of the structure).

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