Qing Shi, Qi-Long Zhang*, Hong Xu and Ya-Li Huang

Crystal structure of 3,3',3''-((1*E*,1'*E*,1''*E*)-((nitrilotris(ethane-2,1-diyl))tris(azaneylylidene))tris(methaneylylidene))tris(4-hydroxy-1-naphthaldehyde) monohydrate, $C_{42}H_{36}N_4O_6 \cdot H_2O$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.24 × 0.23 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.09 mm ⁻¹
Diffractometer, scan mode:	BRUKER APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	47,868, 6780, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 5360
$N(\text{param})_{\text{refined}}$:	495
Programs:	Olex2 [1], Bruker [2], Shelx [3], Diamond [4]

The molecular 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.

<https://doi.org/10.1515/ncrs-2021-0120>

Received March 31, 2021; accepted April 12, 2021;

published online April 26, 2021

Abstract

$C_{42}H_{36}N_4O_7$, triclinic, $P\bar{1}$ (no. 2), $a = 11.8563(6)$ Å, $b = 12.6263(6)$ Å, $c = 13.4492(6)$ Å, $\alpha = 113.563(2)^\circ$, $\beta = 96.740(2)^\circ$, $\gamma = 104.429(2)^\circ$, $V = 1733.07(15)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0470$, $wR_{\text{ref}}(F^2) = 0.1248$, $T = 301.72$ K.

CCDC no.: 2076784

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Source of material

To a solution of 1-naphthol (1 g, 6.9 mmol) in trifluoroacetic acid (10 mL) was added hexamethylenetetramine (1.94 g, 13.8 mmol). The above mixture was heated and stirred for about 1 h. Then concentrated sulfuric acid with a concentration of 33% (10 mL) was added to the stirred solution. The reaction mixture was then stirred and heated for 1 h. Then water was added and the whole solution was extracted by ethyl acetate (30 mL × 2). The mixture was washed with brine and dried and filtered by adding anhydrous magnesium sulfate. The reaction mixture is further purified by column chromatography on silica gel, using ethyl acetate: *n*-hexane (3:7) as the eluant to afford 1-hydroxy-2,4-diformylnaphthalene as yellow oil. To the solution, 1-hydroxy-2,4-diformylnaphthalene (0.60 g, 3 mmol) in 50 mL ethanol was added tri (2-aminoethyl)

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
O1	0.67282 (11)	0.17824 (11)	−0.05327 (10)	0.0549 (3)
O2	0.6140 (2)	−0.15380 (18)	0.20935 (17)	0.1136 (7)
O4	0.56490 (10)	0.41825 (11)	0.38665 (9)	0.0540 (3)
O5	0.85768 (14)	0.40747 (13)	0.36701 (11)	0.0694 (4)
O6	1.01414 (17)	−0.07558 (14)	0.23454 (16)	0.0928 (5)
N1	0.59053 (11)	0.34105 (11)	0.08463 (11)	0.0437 (3)
H1	0.6117	0.3148	0.0225	0.052*
N2	0.76003 (11)	0.59836 (11)	0.22108 (10)	0.0415 (3)
N3	0.74550 (12)	0.61887 (12)	0.45091 (11)	0.0451 (3)
H3	0.6848	0.5629	0.3989	0.054*
N4	0.90252 (13)	0.43894 (13)	0.19194 (12)	0.0516 (3)
H4	0.8802	0.4655	0.2534	0.062*
C1	0.73993 (17)	−0.20695 (16)	−0.08058 (17)	0.0616 (5)
H1A	0.7592	−0.2785	−0.1001	0.074*
C2	0.70537 (15)	−0.15823 (15)	0.01654 (16)	0.0526 (4)
H2	0.7016	−0.1971	0.0626	0.063*
C3	0.67525 (13)	−0.04999 (13)	0.04830 (13)	0.0402 (3)
C4	0.63472 (14)	0.00249 (15)	0.14884 (13)	0.0446 (4)
C5	0.61104 (14)	0.10929 (14)	0.17492 (13)	0.0431 (3)
H5	0.5863	0.1427	0.2404	0.052*
C6	0.62166 (12)	0.17220 (13)	0.10878 (12)	0.0375 (3)
C7	0.59061 (13)	0.27939 (13)	0.14202 (12)	0.0406 (3)
H7	0.5686	0.3081	0.2096	0.049*
C8	0.55727 (15)	0.45134 (15)	0.11765 (15)	0.0504 (4)
H8A	0.5375	0.4724	0.1896	0.060*
H8B	0.4867	0.4367	0.0633	0.060*
C9	0.65926 (15)	0.55664 (14)	0.12552 (14)	0.0498 (4)
H9A	0.6868	0.5310	0.0572	0.060*
H9B	0.6301	0.6240	0.1326	0.060*
C10	0.75461 (17)	0.70437 (14)	0.31734 (14)	0.0506 (4)
H10A	0.6712	0.6981	0.3161	0.061*
H10B	0.7928	0.7781	0.3110	0.061*
C11	0.81524 (17)	0.71464 (15)	0.42733 (14)	0.0531 (4)
H11A	0.8948	0.7082	0.4247	0.064*
H11B	0.8241	0.7939	0.4869	0.064*
C12	0.76748 (14)	0.61120 (14)	0.54377 (13)	0.0440 (4)
H12	0.8319	0.6725	0.6009	0.053*
C13	0.70084 (14)	0.51669 (14)	0.56429 (12)	0.0411 (3)
C14	0.60062 (13)	0.41909 (14)	0.47886 (12)	0.0419 (3)
C15	0.54290 (14)	0.31796 (14)	0.50257 (13)	0.0445 (4)
C16	0.45017 (16)	0.21765 (17)	0.41887 (15)	0.0571 (4)
H16	0.4248	0.2179	0.3509	0.069*
C17	0.39626 (19)	0.11893 (19)	0.43580 (18)	0.0708 (6)
H17	0.3345	0.0527	0.3798	0.085*
C18	0.4344 (2)	0.11853 (19)	0.53676 (18)	0.0728 (6)
H18	0.3981	0.0512	0.5479	0.087*
C19	0.87199 (16)	0.10065 (18)	0.50848 (18)	0.0615 (5)
H19	0.8667	0.0538	0.5474	0.074*
C20	0.91004 (15)	0.06424 (15)	0.41139 (17)	0.0543 (4)
H20	0.9301	−0.0071	0.3854	0.065*
C21	0.91929 (13)	0.13297 (14)	0.35022 (14)	0.0437 (4)
C22	0.95756 (14)	0.09777 (14)	0.24645 (14)	0.0467 (4)
C23	0.95906 (14)	0.16782 (14)	0.19058 (14)	0.0466 (4)
H23	0.9816	0.1425	0.1231	0.056*
C24	0.92879 (13)	0.27546 (14)	0.22882 (13)	0.0432 (3)

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C25	0.93273 (14)	0.34164 (15)	0.16545 (14)	0.0477 (4)
H25	0.9589	0.3132	0.1001	0.057*
C26	0.90287 (18)	0.50816 (18)	0.12679 (16)	0.0585 (5)
H26A	0.8428	0.4589	0.0564	0.070*
H26B	0.9808	0.5284	0.1105	0.070*
C27	0.87601 (16)	0.62363 (16)	0.19195 (15)	0.0527 (4)
H27A	0.9392	0.6747	0.2600	0.063*
H27B	0.8753	0.6684	0.1478	0.063*
C28	0.68638 (13)	0.00916 (13)	−0.02121 (12)	0.0394 (3)
C29	0.72153 (16)	−0.04322 (15)	−0.12058 (14)	0.0523 (4)
H29	0.7280	−0.0048	−0.1670	0.063*
C30	0.74651 (18)	−0.15052 (17)	−0.15024 (16)	0.0632 (5)
H30	0.7679	−0.1855	−0.2173	0.076*
C31	0.66041 (13)	0.12407 (13)	0.00769 (12)	0.0391 (3)
C32	0.6099 (2)	−0.0547 (2)	0.22167 (19)	0.0730 (6)
H32	0.5881	−0.0097	0.2857	0.088*
C33	0.73386 (15)	0.51555 (15)	0.66757 (12)	0.0454 (4)
H33	0.7973	0.5810	0.7223	0.054*
C34	0.67810 (15)	0.42366 (15)	0.69214 (13)	0.0469 (4)
C36	0.58160 (15)	0.31893 (15)	0.60675 (13)	0.0468 (4)
C37	0.52430 (18)	0.21533 (18)	0.62054 (17)	0.0626 (5)
H37	0.5481	0.2128	0.6877	0.075*
C38	0.88971 (15)	0.31522 (15)	0.33144 (14)	0.0471 (4)
C39	0.88716 (14)	0.23985 (15)	0.39186 (14)	0.0450 (4)
C40	0.84899 (17)	0.27474 (18)	0.49113 (16)	0.0580 (4)
H40	0.8283	0.3457	0.5183	0.070*
C41	0.84143 (17)	0.20636 (19)	0.54918 (18)	0.0632 (5)
H41	0.8160	0.2308	0.6152	0.076*
C42	0.99614 (17)	−0.00763 (16)	0.19591 (18)	0.0621 (5)
H42	1.0087	−0.0255	0.1248	0.074*
O3 ^a	0.7964 (2)	0.5211 (2)	0.87907 (15)	0.0734 (8)
C35A ^b	0.724 (3)	0.425 (2)	0.800 (2)	0.0602 (18)
H35A ^b	0.6984	0.3542	0.8096	0.072*
O3A ^b	0.6662 (6)	0.3918 (5)	0.8569 (4)	0.096 (2)
C35 ^a	0.7162 (12)	0.4418 (9)	0.8064 (11)	0.0602 (18)
H35 ^a	0.7905	0.5011	0.8467	0.072*
O1W ^c	1.1141 (3)	−0.2607 (3)	0.1164 (3)	0.0865 (7)
H1WA ^c	1.1767	−0.2286	0.1001	0.130*
H1WB ^c	1.0670	−0.2215	0.1104	0.130*
O1X ^d	1.1651 (4)	−0.2285 (4)	0.1835 (4)	0.0865 (7)
H1XA ^d	1.1426	−0.1661	0.2104	0.130*
H1XB ^d	1.2338	−0.2080	0.1707	0.130*

^aOccupancy: 0.672(4), ^boccupancy: 0.328(4), ^coccupancy: 0.561(4), ^doccupancy: 0.439(4).

amine (0.15 g, 1 mmol). The reaction mixture was refluxed for 8 h, then the solution was cooled to room temperature. The yellow precipitated residue was removed from the solution by filtration and then washed with ethanol and trichloromethane three times. Then a share of the product (0.15 mmol) was dissolved in 20 mL DMF solution. Single crystals were obtained from DMF by slow evaporation at room temperature.

Experimental details

Using Olex2 [1], the structure was solved using Charge Flipping and refined with the ShelXL [3] refinement. All hydrogen atoms were positioned geometrically, with the $d(C-H) = 0.97-0.99 \text{ \AA}$, $U_{iso}(H) = 1.2$ times $U_{eq}(C)$ and $U_{iso}(H) = 1.5$ times $U_{eq}(O)$.

Comment

Naphthaldehyde based nitrogen rich Schiff bases bear excellent coordinating abilities to act as either multi-dentate ligands or bridging blocks in supramolecular chemistry and have been highlighted in the literature due to novel structural architectures as well as potential applications of their complexes [5]. In the crystal structure of the title compound, the asymmetric unit of the title compound consists of one formula unit of the target molecule and one water molecule. The bond lengths and bond angles are in the normal ranges [6]. The crystal structure shows that the hydrogen on the hydroxyl oxygen atom of phenol moiety is transferred to the nitrogen atom of imine to form keto-enamine [6]. There are intramolecular hydrogen bonds (for example: $N1-H1 \cdots O1$, $N3-H3 \cdots O4$, $N4-H4 \cdots O5$, $C7-H7 \cdots O4$) in the molecules. Through the hydrogen bond of $O1W-H1WA \cdots O1$, $O1W-H1WB \cdots O6$ the interaction between the target and water molecules extends into a dimer structure. The water

molecule and one of the aldehyde groups show a disorder.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was supported by and the National Natural Science Foundation of China (22065009, 22066007) and Preventive Medicine (No. 2017[85]), Science and Technology Foundation of Guizhou Province (grant numbers [2019]2792, [2018]5779-14).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, 42, 339–341.
2. Bruker. APEX2, SAINT and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
4. Brandenburg K. DIAMOND. Visual Crystal Structure Information System. Ver. 4.0; Crystal Impact: Bonn, Germany, 2015.
5. Naskar B., Modak R., Mait D. K., Drew M. G. B., Bauza A., Frontera A., Mukhopadhyay C. D., Mishra S., Saha K. D., Goswami S. A Schiff base platform: structures, sensing of Zn(II) and PPI in aqueous medium and anticancer activity. *Dalton Trans.* 2017, 46, 9498–9510.
6. Park H., Kim J., Kwon E., Kim T. H. Crystal structure of flucetosulfuron. *Acta Crystallogr.* 2017, E73, 1439–1442.